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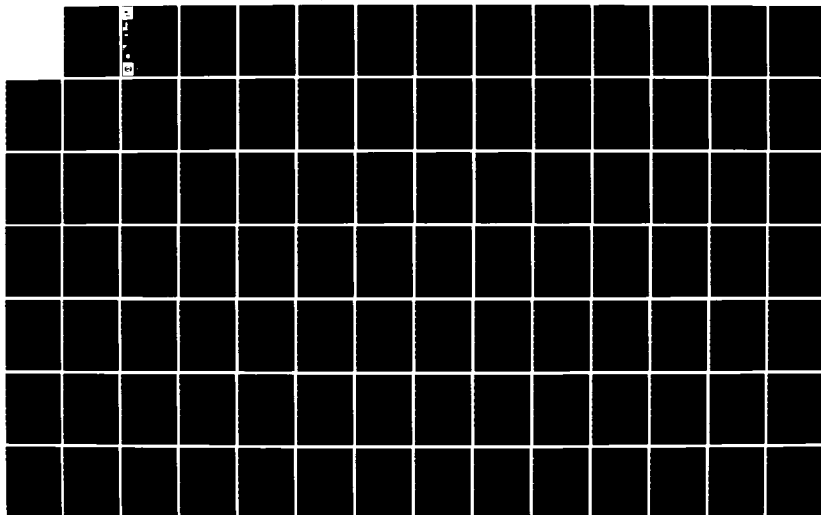
SIMPLIFIED PROCEDURE FOR CALCULATING CHEMICAL DOSES FOR 1/3
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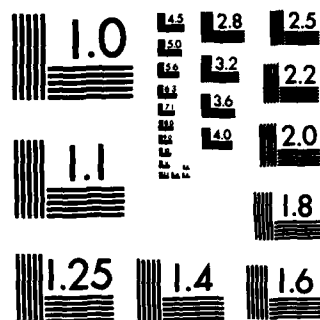
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TECHNICAL REPORT EL-84-6

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SIMPLIFIED PROCEDURE FOR CALCULATING CHEMICAL DOSES FOR WATER STABILIZATION FOR PREVENTION OF INTERNAL CORROSION AND SCALING

by

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Environmental Laboratory

DEPARTMENT OF THE ARMY
Waterways Experiment Station, Corps of Engineers
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June 1984
Final Report

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The procedures described in this report are superior to Caldwell-Lawrence diagrams or indices (used to determine if water is stable) in that the procedures can directly yield chemical doses rather than requiring a trial-and-error solution. The procedures are based on numerically solving the equations describing calcium carbonate equilibrium. The data required to use the procedure include a description of raw water calcium hardness, alkalinity, pH, temperature, and total dissolved solids.

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PREFACE

The study described in this report was sponsored by the Office, Chief of Engineers, U. S. Army, under the Water Supply and Conservation Program, Work Unit 31733, Water Supply System Design. General oversight of the Water Supply and Conservation Program has been assigned to the U. S. Army Engineer Institute for Water Resources. Responsibility for portions of the program have been assigned to the U. S. Army Engineer Waterways Experiment Station (WES) under the direction of the Environmental Laboratory (EL).

This report was prepared by Dr. Joe M. Morgan and Dr. Thomas M. Walski of the Water Resources Engineering Group and Dr. Marion W. Corey of Mississippi State University under the direction of Mr. Michael R. Palermo, Chief, Water Resources Engineering Group; Mr. Andrew J. Green, Chief, Environmental Engineering Division; and Dr. John Harrison, Chief, EL. Ms. Katherine Smart and Ms. Jane Dornbush of the Water Resources Engineering Group made especially valuable contributions to the work.

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SIMPLIFIED PROCEDURE FOR CALCULATING CHEMICAL DOSES
FOR WATER STABILIZATION FOR PREVENTION
OF INTERNAL CORROSION AND SCALING

PART I: INTRODUCTION

Background

1. Internal corrosion of metallic elements of water distribution systems and appurtenances is an electrochemical process whereby metal dissolves. Metallic ions thus formed may simply be carried away by flowing water, or may react with other dissolved constituents to form various insoluble precipitates. The precipitates may themselves be carried away with the flow, but are frequently deposited on nearby surfaces. Over a long period of time, the net result is that metallic mass is lost and deposits of corrosion products accumulate. The effect of the former is to weaken the pipe or appurtenance because the thickness of the metal is decreased, while that of the latter is to increase flow resistance because surface roughness is increased. As pipes and appurtenances weaken, breaks become more and more likely and repair or replacement eventually becomes necessary. This can be expensive and is often complicated by the difficulty in locating breaks in system components that are hidden from view. Increases in flow resistance lead to reduced flow rates and increased pumping costs. Possible remedies include cleaning and lining, increasing the available head, or installing parallel pipes. All of these solutions can be expensive.

2. It is interesting to note that even nonmetallic materials such as cement, concrete, and asbestos-cement can corrode. The process is, of course, considerably different than that applicable to corrosion of metals, but the results are similar. Scaling can affect any kind of piping material, including plastic. In cases in which the distribution system is lined with a corrosion resistant material, corrosion can cause significant problems in customer plumbing. An excellent illustration of this was noted by Hudson and Gilcreas (1976) who observed that, for a certain distribution system composed principally of reinforced concrete, asbestos-cement, and cement-lined cast iron pipe, measured values of the Hazen-Williams coefficient (C-factor) declined from

about 130 to about 80 in only 5 years time as the result of exposure to corrosive waters.

Economics of the problem

3. Internal corrosion of water distribution systems and residential, commercial, and industrial plumbing systems is an economic, nuisance, and public health problem of national significance. For example, Bennett et al. (1979) reported that a National Bureau of Standards study of corrosion concluded that the annual cost of corrosion of water distribution systems in the United States is in the neighborhood of \$700 million, and that some 20 percent of this amount (\$140 million) can be avoided by the implementation of corrosion control measures. Other researchers (Hudson and Gilcreas 1976) suggest an avoidable corrosion cost figure as high as \$375 million per year. While gross estimates such as these may, of course, be subject to considerable error, they do serve to emphasize the general magnitude of the problem. A much more detailed study of a large metropolitan distribution system (Ryder 1980) revealed an annual cost of internal corrosion of approximately \$400,000. Furthermore, it was determined that the annual costs of corrosion of the attached residential, commercial, and industrial plumbing systems totaled about \$7 million. If this ratio of distribution system costs to customer costs (i.e. \$400,000/\$7 million) is applicable to the gross national figures quoted above, the total bill for internal corrosion associated with public water distribution systems may be as high as \$12 billion per year (i.e. \$700 million \times (71.4)).

Effect on public health

4. Since the enactment of the Safe Drinking Water Act (Public Law (PL) 92-523, 42 USC: 300f. et seq.) and the development of the regulations required to implement it, there has been increasing concern over the quality of public water supplies and the possible health effects of various chemical and biological contaminants. This general climate has prompted in-depth studies aimed at developing a better understanding of changes in water quality that may occur after water leaves a treatment facility, but before it is delivered to the ultimate users. As would be expected, the corrosion process has been found to be a major contributor to such quality changes.

5. The full extent of the adverse impact of internal corrosion on the public health of the nation is not known. However, after exhaustive review of the applicable literature, and careful analysis of data gathered in several

case studies, the Safe Drinking Water Committee of the National Research Council (NRC) concluded (NRC 1982) that metallic corrosion products in water distributed to consumers can originate from water mains, service lines, and interior plumbing. Lead was noted to be worthy of particular concern since its adverse effects on human health are at least partially understood. However, other metals such as iron, copper, zinc, and cadmium, as well as asbestos fibers released by deteriorating asbestos-cement pipe, were identified as posing potential problems. Furthermore, it was observed that finished water quality is an important factor influencing corrosion rates. The Committee also observed that, while chemical additives such as corrosion inhibitors can be used to mitigate corrosion to some extent, they should be used judiciously to minimize human exposures.

Nuisance problems

6. Nuisance problems associated with corrosion in water distribution systems and individual plumbing systems include staining of fixtures, interference with laundry and cleaning operations, and loss of aesthetic qualities related to color, taste, and odor. In many cases, bacteria such as *Crenothrix*, *Clonothrix*, *Gallionella*, and *Thiobacillus ferrooxidans* contribute significantly to consumer complaints about "red water." The latter two types are especially important since they are apparently capable of using ferrous iron as a sole energy source (Gaudy and Gaudy 1980).

Legal aspects

7. The U. S. Environmental Protection Agency (EPA) has recognized the importance of problems associated with corrosion in the National Interim Primary Drinking Water Regulations (40 CFR 141). Specifically, these regulations establish maximum contaminant levels (MCLs) for various substances, and make it the responsibility of water suppliers to deliver water that meets the requirements of the regulations to the "free flowing outlet of the ultimate user." Contaminants added to water as a result of corrosion in either the supplier's distribution system or the user's plumbing system are covered by these provisions. Thus, the supplier bears the responsibility of ensuring that corrosion does not result in unacceptable water quality.

Summary

8. The discussion presented above makes it clear that internal corrosion is an important potential water distribution problem. However, local variations in water quality, distribution system design and operation, pipe

materials, record keeping, etc., make it somewhat more difficult to establish the true extent of the impact of corrosion. Perhaps the most comprehensive national data come from a large-scale cooperative health study involving the EPA; the National Heart, Lung, and Blood Institute; the National Center for Health Statistics; and the Bureau of the Census. Water quality data gathered as a part of this effort (Millette et al. 1980) indicated that about 70 percent of the water utilities surveyed distributed moderately to highly aggressive (corrosive) water. This conclusion was based upon the results of analyses performed on about 1300 water samples taken from 135 representative water systems across the United States. Collectively, these systems serve over 40 million persons. Study locations were selected by a random sampling procedure and, therefore, it may be presumed that there was no bias toward especially corrosive waters. The results compare favorably with those of Dufor and Becker (1964) which indicated that about one half of the 100 largest U. S. cities were distributing water that could be considered corrosive. In a very early study, Langelier (1936) noted that the majority of large American cities studied were distributing corrosive water. Thus, it would appear that the distribution of corrosive water has been, and is today, a relatively common practice in this country.

Stabilization and Corrosion Control

9. Several means of minimizing internal corrosion are available: the use of corrosion-resistant pipe materials and/or linings, insulation of dissimilar metals, impressed cathodic protection, and treatment of the water to render it relatively noncorrosive. With regard to the latter approach, corrosion "inhibitors" (mostly organic compounds) may be used, or the alkalinity, calcium hardness, and pH of the water may be adjusted so as to deposit and maintain a thin protective scale layer on the interior of pipes and appurtenances. The protective scale layer is composed of calcium carbonate (CaCO_3) along with various other constituents, depending upon site-specific factors. The latter approach is variously referred to as "stabilization," "chemical stabilization," "calcium carbonate stabilization," or "water conditioning" and is generally beneficial even if other corrosion control measures are employed.

10. Failure to properly stabilize water can lead to excessive scale

deposits which reduce carrying capacity and may eventually clog pipes and render appurtenances inoperable. Thus, stabilization is important in its own right, outside the context of corrosion control. Given this situation, stabilization should be of concern for virtually every supplier of potable water, and for many industrial and commercial process applications as well.

Previous Approaches to Stabilization

11. Over the years, stabilization has received considerable attention in the water supply literature. A major portion of that literature deals with the attempts of various researchers to develop a simple, dependable index that may be used to determine if a water is stable or unstable. The best known of these, the saturation index, was introduced by Langelier in 1936 (Langlier 1936). The saturation index has been used widely, but is well known to be an imperfect indicator of stability (Benefield, Judkins, and Weand 1982; Loewenthal and Marais 1982; Stumm and Morgan 1981). The principal shortcoming is that it cannot be used directly to determine the chemical doses needed to achieve the desired stability. The same is true of the host of other indices that have been presented (Singley 1981).

12. Since, as is subsequently described, the carbonate system is rather complex, and the simultaneous solution of many equilibrium expressions by manual means is tedious at best, graphical procedures for estimating the quantities of chemicals needed to stabilize water have been developed (Langelier 1946; Caldwell and Lawrence 1953; Merrill and Sanks 1977; Loewenthal and Marais 1982). The most popular, by far, are the so called "Caldwell-Lawrence diagrams." These diagrams, discussed in great detail by Merrill and Sanks (1977) and Loewenthal and Marais (1982), are very useful and can be utilized to solve a wide variety of water chemistry problems. Their chief limitations, from the viewpoint of a user wishing to estimate the chemical doses required to stabilize a water, are that they are very complex, are overwhelming in appearance, and an often tedious trial-and-error solution approach must be used for virtually all practical applications. The complexity of the Caldwell-Lawrence diagrams makes them confusing, tends to intimidate many potential users, and, thus, mitigates against their general acceptance and use. Even experienced users often have difficulty because there are so many lines on the diagrams that it is easy to lose one's place or inadvertently shift to the wrong line

in the middle of a problem. Another difficulty is that the precision with which the diagrams may be read is quite low, especially in some regions.

Purpose of this Study

13. As noted above, principal difficulties associated with stabilization are that the chemistry involved is rather complex and there is no simple, straightforward analytical procedure that can be used to determine, in advance, exactly how the quality of a water should be altered to achieve the desired result. The effort described in this report was initially undertaken with the goal in mind of developing such a procedure. In the final analysis, two separate, but related, procedures were developed. Each of these is described briefly below, and in greater detail in subsequent sections.

14. Many water treatment plants are, or soon will be, equipped with sophisticated microcomputers. Therefore, a microcomputer program was written to calculate the quantities of chemicals that should be added to a water to stabilize it to virtually any desired condition. The program is very user friendly, requires input data of the type that is almost always available at treatment plants, and can produce several types of output, depending upon the desires of the user. The program is available in a convenient diskette format suitable for either the Apple II or IBM Personal Computer, and will be of interest to design engineers and planners as well as water treatment plant operating personnel. This program is described in detail in Part V of this report.

15. While the use of microcomputers in the water utility industry is increasing rapidly, for the foreseeable future there will remain a need for manual procedures. Thus, a computer program was written and linked to an automatic plotter to draw water stabilization diagrams that can be used in a simple, straightforward manner to estimate the quantities of chemicals needed to stabilize a water. The set of diagrams presented in Appendix A may be used with acceptable accuracy for most potable waters. If desired, the plotting program may be used to draw customized diagrams for specific applications. The rationale used in developing the plotting program and constructing the diagrams is presented in Part III. The basic chemistry needed to understand how the diagrams were constructed is presented in Part II. These diagrams should prove especially useful to operating personnel since they can often be used with acceptable accuracy without interpolation or intermediate

calculations. They will also be useful to engineers and planners desiring to estimate water treatment costs for preliminary design or planning purposes.

16. The water stabilization diagrams developed as part of the work reported herein are much easier to use than the Caldwell-Lawrence diagrams. They are less confusing, in that far fewer lines are printed on each diagram, and they may be used directly without any trial-and-error procedure. While interpolation may be required for some problems, this is not a great limitation since the same is true of the Caldwell-Lawrence diagrams. Simplicity has its price, of course. In this instance it has been achieved at the expense of less flexibility with respect to the types of water chemistry problems that may be solved. However, for water stabilization problems, the diagrams presented in this report are far easier to use than any previously published method.

17. It is assumed that the vast majority of readers will have no particular interest in the plotting program itself; the program is available from WES. Those who wish to adapt the program to their own use, or who would like to have specific diagrams generated for them, should contact:

U. S. Army Engineer Waterways Experiment Station
ATTN: Dr. Thomas M. Walski WESEE-R
P. O. Box 631
Vicksburg, Miss. 39180

Effective Use of this Report

18. It is anticipated that many readers of this report may have a considerably greater interest in using the water stabilization diagrams and microcomputer programs than in reading about the chemical theory upon which they are based. Thus, those desiring to use the diagrams may wish to proceed directly to Appendix A. The instructions provided there are sufficient for most applications; however, it may be helpful to also consider the examples presented in Part IV. Similarly, readers having interests in the microcomputer programs may wish to proceed directly to Part V and, hence, to Appendix B and/or C. Those desiring to understand the chemical theory involved and the rationale used in developing the diagrams and microcomputer programs should proceed through the following sections sequentially as they are presented.

PART II: REVIEW OF FUNDAMENTAL CHEMISTRY

Introduction

19. A water that tends to neither precipitate nor dissolve calcium carbonate (CaCO_3) may be said to be "stable" (i.e. exactly saturated) with respect to calcium carbonate. The same water may, of course, be unstable (i.e. will tend to form or dissolve precipitates) with respect to other chemical species. However, in the potable water supply industry calcium carbonate is the principal precipitate of concern for finished (treated) waters and, thus, "stability" is usually defined solely in terms of calcium carbonate.

20. Calcium carbonate stability is important because waters that are supersaturated will tend to deposit thick layers of scale on the inside of pipes and appurtenances, and thus reduce carrying capacity. On the other hand, waters that are undersaturated will tend to dissolve existing scale deposits and, if no scale is present, will tend to promote corrosion of both ferrous and nonferrous metals. Undersaturated waters will also tend to promote the deterioration of certain nonmetallic components such as asbestos-cement and concrete pipes and cement-based pipe linings.

Stabilization for Potable Water Supply

21. As practiced in the potable water supply industry, water stabilization usually involves careful adjustment of the alkalinity, calcium hardness, and pH of finished water to deposit and maintain a thin layer of calcium carbonate scale on the inside surfaces of pipes and appurtenances. The scale layer prevents direct contact between the water and the pipe material and, thus, interrupts the corrosion cycle. It has been known for a long time that, at least for some waters, other precipitates such as siderite (FeCO_3), goethite (FeOOH), and magnetite (Fe_3O_4) may play important roles in the formation of protective scales. This was recently emphasized by Sontheimer, Kölle, and Snoeyink (1981) who proposed a highly simplified model for the development of corrosion-resistant scales based on the precipitation of siderite. However, it is possible to understand the elements of water stabilization from consideration of calcium carbonate alone. For the sake of clarity, this approach is taken below.

Basic Carbonate Chemistry

22. The carbonate system includes carbon dioxide (CO_2), carbonic acid (H_2CO_3), bicarbonate ion (HCO_3^-), carbonate ion (CO_3^{2-}), as well as the hydroxide (OH^-) and hydrogen (H^+) ions, and associated precipitates such as CaCO_3 and FeCO_3 . It is the most important chemical system for virtually all natural waters. For example, carbon dioxide in the atmosphere, or formed in the soil as a by-product of microbiological metabolism, is readily absorbed by water to form a solution of carbonic acid that may, depending upon pH and exact chemical composition, react with alkaline materials (mostly carbonates) found in rocks to dissolve them, or deposit various precipitates. By these means, carbonate and bicarbonate ions may be added to, or removed from, the water. The chemical reactions involved are very important in regulating the pH and chemical composition of both natural and treated waters. Excellent discussions of the chemistry of the carbonate system are presented by Stumm and Morgan (1981); Benefield, Judkins, and Weand (1982); Loewenthal and Marais (1982); and Snoeyink and Jenkins (1980).

Precipitation/ dissolution of calcium carbonate

23. The precipitation or dissolution of solid calcium carbonate may be described by the following simple chemical reaction between dissolved species on the left and undissolved solids on the right. (The subscript (s) denotes a



solid.) If the product of the concentrations of the calcium (Ca^{2+}) and carbonate (CO_3^{2-}) ions exceeds some critical value, called the solubility product, calcium carbonate precipitate may be expected to form. If, on the other hand, the ionic concentration product is less than the solubility product, no precipitate may be expected to form and, in fact, any that is present will tend to dissolve until the resulting ion product is exactly equal to the solubility product. Thus, for a solution that is exactly saturated (i.e. at equilibrium) with calcium carbonate, we may write

$$K_s = (\text{Ca}^{2+})(\text{CO}_3^{2-}) \quad (2)$$

where

K_s = solubility product for calcium carbonate

(Ca^{2+}) = equilibrium calcium ion activity

(CO_3^{2-}) = equilibrium carbonate ion activity

By convention, the ionic activities are usually expressed in terms of moles per litre, and K_s is expressed in compatible units. The solubility product, like other thermodynamic equilibrium constants, is a function of both temperature and total ionic strength. Again by convention, reported values are usually for 25° C and an "ideal" solution. (In an ideal solution, ions do not interfere with one another; thus there is no ionic strength effect.) Of course, it is not possible, strictly speaking, to have an ideal solution. Nevertheless, for dilute solutions (such as drinking water), the assumption that the effect of ionic strength is insignificant is often made. In times past, when hand calculations were required, this could, perhaps, be justified. Today, however, there is little to recommend such a simplification.

24. Larson and Boswell (1942), building upon the work of others, developed the following expression relating the solubility product of calcium carbonate to temperature:

$$pK_s = 0.01183(T) + 8.03 \quad (3)$$

where

pK_s = the negative log (base 10) of the solubility product for calcium carbonate K_s corrected for temperature

T = temperature, °C ($0 \leq T \leq 80$)

Thus, the solubility product is given by

$$K_s = 10^{-pK_s} \quad (4)$$

The effect of ionic strength may be taken into account by rewriting Equation 2 as follows:

$$K_s = G_D[Ca^{2+}] \times G_D[CO_3^{2-}] \quad (5)$$

where,

[]s = analytical (i.e. actual) molar equilibrium concentrations (not activities)

G_D = activity coefficient for divalent ions

Activity coefficients may be estimated using a modification of the Davies equation (Stumm and Morgan 1981) as shown below

$$\log G = -AZ^2 \left(\frac{\sqrt{IS}}{1 + \sqrt{IS}} - 0.3IS \right) \quad (6)$$

where,

G = activity coefficient for the chemical species of interest (the subscripts M, D, and T are used to denote monovalent, divalent, and trivalent ions, respectively)

$A = 1.82 \times 10^6 [(D)(T + 273)]^{-3/2}$

T = temperature, °C

D = dielectric constant for water (generally taken to have a value of 78.3)

Z = oxidation number of the chemical species of interest

IS = total ionic strength of the solution, moles/l

The IS (in moles per litre) may be approximated as follows (Langelier 1936; Kemp 1971)

$$IS = 2.5 \times 10^{-5} (TDS) \quad (7)$$

where TDS = total dissolved solids, mg/l,

or

$$IS = 1.675 \times 10^{-5} (EC) \quad (8)$$

where EC = electrical conductance at 20° C, $\mu\text{mho/cm}$. Equation 7 generally provides a reasonable estimate of IS for waters having TDS concentrations lower than about 1000 mg/l. Modifications that account for the presence of nonionic constituents such as silica have been proposed (Kemp 1971), but there seems to be little practical reason to be overly concerned with the accuracy of the estimation of ionic strength. However, if a complete water analysis is available, total ionic strength may be determined exactly as

$$IS = 0.5 \sum_{i=1}^n C_i Z_i^2 \quad (9)$$

where

C_i = analytical (i.e. actual) concentration of the i^{th} ionic species, moles/l

Z_i = oxidation number of the i^{th} ionic species

25. Equation 5 can be rearranged to yield

$$\frac{K_s}{G_D^2} = [Ca^{2+}][CO_3^{2-}] \quad (10)$$

The left side of Equation 10 represents the effective solubility product K'_s which includes the effects of both temperature and ionic strength, and may be used with chemical species concentrations (not activities) expressed as moles per litre. That is,

$$K'_s = \frac{K_s}{G_D^2} \quad (11)$$

Careful inspection of Equations 3, 4, 6, and 10 reveals that, for calcium carbonate, solubility increases with increasing ionic strength but decreases with increasing temperature. This latter characteristic has important implications for hot water applications since, as a water is heated, it will tend more toward supersaturation (and thus precipitation).

26. Most engineers, technicians, and operating personnel in the potable water supply industry are accustomed to expressing alkalinity and calcium and magnesium hardness concentrations in terms of milligrams per litre as $CaCO_3$ rather than moles per litre. Thus, it is often convenient to define the solubility product for calcium carbonate in such a way as to facilitate the use of these common units of expression. To do this, K'_s may be modified as follows:

$$K'_{sc} = K'_s \times 10^6 \quad (12)$$

where K'_{sc} = solubility product for calcium carbonate, corrected for temperature and ionic strength, for use with chemical species concentrations expressed in terms of milligrams per litre as $CaCO_3$.

Alkalinity and acidity

27. The alkalinity of a water may be defined in a general way as the capacity of the water to neutralize an acid. Acidity may be similarly defined as the capacity of a water to neutralize a base. While these definitions are good from a conceptual viewpoint, they lack a practical focus. For the overwhelming majority of natural waters, however, alkalinity may be assumed to result from the presence of a strong base (i.e. hydroxyl ions, OH^-) in a carbonic acid (H_2CO_3) solution. Alkalinity can be conveniently measured in the laboratory by titrating a sample containing a known volume of the water against a strong acid standard (American Public Health Association (APHA) 1980; Benefield, Judkins, and Weand 1982; Loewenthal and Marais 1982; Sawyer and McCarty 1978). On the other hand, acidity, which may be assumed to result from the presence of a strong acid (i.e. the hydrogen ion, H^+) in a carbonic acid solution, is much less convenient to determine analytically. However, if pH and alkalinity are known, acidity can be readily determined mathematically. Alkalinity and pH are both routinely determined in laboratories at water treatment plants.

Principal reactions

28. Carbonic acid is a weak diprotic acid that dissociates in two distinct steps. Reactions of interest for the carbonic acid system are presented below:



Reaction 13 indicates that, in a water solution, carbon dioxide may exist either as a dissolved gas or in the form of molecules of carbonic acid. In virtually all situations of interest in the potable water supply industry, the vast majority of the carbon dioxide is present as dissolved gas. However, it is almost impossible to distinguish the two forms. Thus, it is common practice to let the carbonic acid shown in Reaction 14 represent the total of the

carbonic acid and the dissolved carbon dioxide gas. This convention is followed herein.

Dissociation of water

29. Reaction 15 indicates that the water molecule itself can dissociate to form equal amounts of strong acid (H^+) and strong base (OH^-), and that reactions between strong acids and strong bases result in the formation of water molecules. By convention, the thermodynamic equilibrium constant for this reaction may be written as

$$K_w = (H^+) \times (OH^-) \quad (17)$$

where

K_w = thermodynamic equilibrium constant for water
 (H^+) = equilibrium hydrogen ion activity, moles/l
 (OH^-) = equilibrium hydroxyl ion activity, moles/l

30. Harned and Hamer (1933) determined that the influence of temperature on K_w may be quantified as follows

$$pK_w = \frac{4787.3}{T + 273} + 7.1321 \log (T + 273) + 0.010365(T + 273) - 22.801 \quad (18)$$

where

pK_w = negative log (base 10) of the thermodynamic equilibrium constant for water, corrected for temperature
 T = temperature, °C ($0 \leq T \leq 60$)

Thus, we may write

$$K_w = 10^{-pK_w} \quad (19)$$

31. To account for the effects of ionic strength, and facilitate the use of analytical chemical species concentrations in moles per litre, we may rewrite Equation 16 as

$$K_w = G_M[H^+] \times G_M[OH^-] \quad (20)$$

where

[]s = analytical (i.e. actual) molar equilibrium concentrations (not activities)
 G_M = activity coefficient for monovalent ions

Rearranging Equation 18 we have

$$\frac{K_w}{G_M^2} = [H^+][OH^-] \quad (21)$$

The quantity shown on the left side of the equation may be redefined as

$$K'_w = \frac{K_w}{G_M^2} \quad (22)$$

where K'_w = the thermodynamic equilibrium constant for water, corrected for temperature and ionic strength, for use with chemical species concentrations expressed as moles per litre. Finally, we may write

$$K'_{wc} = K'_w \times 2.5 \times 10^{-9} \quad (23)$$

where K'_{wc} = the thermodynamic equilibrium constant for water, corrected for temperature and ionic strength, for use with chemical species concentrations expressed in terms of milligrams per litre as $CaCO_3$.

First dissociation of carbonic acid

32. Equation 14 indicates that an equilibrium exists between carbonic acid (and dissolved CO_2) on the left and hydrogen and bicarbonate ions on the right. The thermodynamic equilibrium constant for this reaction is

$$K_1 = \frac{(H^+)(HCO_3^-)}{(H_2CO_3)} \quad (24)$$

where

- K_1 = the so-called "first dissociation constant" for carbonic acid
- (HCO_3^-) = equilibrium bicarbonate ion activity, moles/l
- (H_2CO_3) = sum of the carbonic acid and dissolved carbon dioxide concentrations (not activities, since neither of these species is ionized), moles/l

Shadlovsky and MacInnes (1935) established that

$$pK_1 = \frac{17.052}{T + 273} + 215.21 \log (T + 273) - 0.12675(T + 273) - 545.56 \quad (25)$$

where

pK_1 = negative log (base 10) of the first dissociation constant for carbonic acid K_1 corrected for temperature

T = temperature, °C ($0 \leq T \leq 38$)

33. Using a procedure similar to that described for the solubility product for calcium carbonate and the thermodynamic equilibrium constant for water, we may write

$$K_1 = 10^{-pK_1} \quad (26)$$

$$K'_1 = \frac{K_1}{G_M^2} \quad (27)$$

$$K'_{1c} = K'_1 \times 2.5 \times 10^4 \quad (28)$$

where K'_1 and K'_{1c} = the first dissociation constant for carbonic acid, corrected for temperature and ionic strength, for use with chemical species concentrations expressed as moles per litre and milligrams per litre as CaCO_3 , respectively.

Second dissociation of carbonic acid

34. Equation 15 shows that the bicarbonate ion can dissociate to form hydrogen and carbonate ions. The equilibrium condition for this reaction can be expressed as

$$K_2 = \frac{(H^+)(CO_3^{2-})}{(HCO_3^-)} \quad (29)$$

where

K_2 = the so-called "second dissociation constant" for carbonic acid

(CO_3^{2-}) = equilibrium carbonate ion activity, moles/l

(HCO_3^-) = equilibrium bicarbonate ion activity, moles/l

Harned and Scholes (1941) showed that

$$pK_2 = \frac{2902.39}{T + 273} + 0.2379(T + 273) - 6.498 \quad (30)$$

where

pK_2 = negative log (base 10) for the second dissociation constant for carbonic acid K_2 corrected for temperature

T = temperature, °C ($0 \leq T \leq 50$)

35. Using a procedure similar to that described for the solubility product of calcium and the thermodynamic equilibrium constant for water, we may write

$$K_2 = 10^{-pK_2} \quad (31)$$

$$K'_2 = \frac{K_2}{G_D} \quad (32)$$

$$K'_{2c} = K'_2 \times 10^5 \quad (33)$$

where K'_2 and K'_{2c} = the second dissociation constant for carbonic acid, corrected for ionic strength, for use with chemical species concentrations expressed as moles per litre and milligrams per litre as CaCO_3 , respectively.

Effects of reactions on alkalinity and acidity

36. Inspection of Equations 14, 15, and 16 reveals that, as the indicated reactions move from right to left, hydrogen ions are removed from solution (i.e. acid is neutralized) by bicarbonate, carbonate, and hydroxyl ions. Thus, given the general definition of alkalinity as the capacity of a water to neutralize an acid, and assuming that the alkalinity of a water results from the presence of a strong base in a carbonic acid solution, we may write the following expression:

$$(\text{ALK}) = (\text{CO}_3^{2-}) + (\text{HCO}_3^-) + (\text{OH}^-) - (\text{H}^+) \quad (34)$$

where

(ALK) = alkalinity of the water

(CO_3^{2-}) = carbonate ion concentration

(HCO_3^-) = bicarbonate ion concentration

(OH^-) = hydroxyl ion concentration

(H^+) = hydrogen ion concentration

Any directly comparable units of expression may be used, for example, equivalents per litre or milligrams per litre as CaCO_3 . If it is desired to express all terms in moles per litre, it is necessary to multiply the (CO_3^{2-}) and (ALK) terms by a factor of two since there are two moles per equivalent for each of these species. (Note: alkalinity is not really a single chemical species, but may be thought of in terms of equivalents of CaCO_3 .)

37. If the reactions shown by Equations 14, 15, and 16 are assumed to be moving from left to right, hydrogen ions are added to solution and, thus, acidity is increased. Therefore, we may write

$$(\text{ACD}) = (\text{H}_2\text{CO}_3) + (\text{HCO}_3^-) + (\text{H}^+) - (\text{OH}^-) \quad (35)$$

where

(ACD) = acidity of the water

(H_2CO_3) = sum of the carbonic acid and dissolved CO_2 gas concentrations

As was the case for Equation 34, comparable units of expression such as equivalents per litre or milligrams per litre as CaCO_3 may be used directly with this expression. If it is desired to express the concentrations as moles per litre, the (H_2CO_3) term must be multiplied by a factor of two since there are two moles of H_2CO_3 per equivalent.

Relationships among alkalinity, acidity, and pH

38. As mentioned previously, the alkalinity of a natural or potable water may be readily determined in the laboratory, but acidity is much more difficult to measure. Fortunately, acidity may be calculated, if the alkalinity and hydrogen ion concentrations are known. The hydrogen ion concentration may be determined from an accurate pH measurement as follows:

$$[\text{H}^+] = \frac{10^{-\text{pH}}}{G_m} \quad (36)$$

where

$[\text{H}^+]$ = hydrogen ion concentration, moles/l

pH = negative log of the hydrogen ion activity, moles/l, as determined by a pH meter

G_m = activity coefficient for a monovalent ion

The activity coefficient must be present in Equation 36 because pH meters

respond to hydrogen ion activity, not concentration. The units of hydrogen ion concentration may be converted to milligrams per litre as CaCO_3 as follows:

$$(\text{H}^+) = [\text{H}^+] \times 5 \times 10^4 \quad (37)$$

where

(H^+) = hydrogen ion concentration, mg/l as CaCO_3

$[\text{H}^+]$ = hydrogen ion concentration, moles/l

39. A simple expression for acidity as a function of alkalinity and hydrogen ion concentration is developed below. This expression is subsequently used in determining the chemical doses required for stabilization.

40. Combining Equation 29, the expression for the second dissociation constant for carbonic acid, with Equations 32 and 33, we can write

$$K'_{2c} = \frac{K_2}{G_m} \times 10^5 = \frac{(\text{H}^+)(\text{CO}_3^{2-})}{(\text{HCO}_3^-)} \quad (38)$$

where all chemical species concentrations are expressed in milligrams per litre as CaCO_3 . Solving for the carbonate ion concentration, we have

$$(\text{CO}_3^{2-}) = \frac{(\text{HCO}_3^-)K'_{2c}}{(\text{H}^+)} \quad (39)$$

Substituting Equation 39 into Equation 34 and solving for (HCO_3^-) , we have

$$(\text{HCO}_3^-) = \frac{(\text{ALK}) - (\text{OH}^-) + (\text{H}^+)}{1 + \frac{K'_{2c}}{(\text{H}^+)}} \quad (40)$$

41. We may also combine Equation 24, the expression for the first dissociation constant of carbonic acid, with Equations 27 and 28 to yield

$$K'_{1c} = \frac{K_1}{G_m^2} \times 2.5 \times 10^4 = \frac{(\text{H}^+)(\text{HCO}_3^-)}{(\text{H}_2\text{CO}_3)} \quad (41)$$

where all concentrations are, again, expressed as milligrams per litre as CaCO_3 . Solving Equation 39 for (HCO_3^-) we have

$$(\text{HCO}_3^-) = \frac{(\text{H}_2\text{CO}_3)K'_{1c}}{(\text{H}^+)} \quad (42)$$

Substituting this expression into Equation 41, and solving for (CO_3^{2-}) , yields

$$(\text{CO}_3^{2-}) = \frac{(K'_{1c})(K'_{2c})(\text{H}_2\text{CO}_3)}{(\text{H}^+)^2} \quad (43)$$

Substituting Equations 42 and 43 into Equation 34 and solving for (H_2CO_3) we have

$$(\text{H}_2\text{CO}_3) = \frac{(\text{ALK}) - (\text{OH}^-) + (\text{H}^+)}{\left[\frac{K'_{1c}}{(\text{H}^+)} \right] \left[1 + \frac{K'_{2c}}{(\text{H}^+)} \right]} \quad (44)$$

Substituting Equations 40 and 44 into Equation 35, replacing the (OH^-) terms with $K'_{wc}/(\text{H}^+)$ (see Equations 17, 22, and 23), and rearranging yields

$$(\text{ACD}) = \frac{\left[(\text{ALK}) - \frac{K'_{wc}}{(\text{H}^+)} + (\text{H}^+) \right]}{\left[1 + \frac{K'_{2c}}{(\text{H}^+)} \right]} \left[1 + \frac{(\text{H}^+)}{K'_{1c}} \right] - \frac{K'_{wc}}{(\text{H}^+)} + (\text{H}^+) \quad (45)$$

which is the general expression for acidity as a function of alkalinity and hydrogen ion concentration. It should be noted that this equation requires that all chemical species concentrations be expressed as milligrams per litre as CaCO_3 . If it is desired to express all the concentrations in terms of equivalents per litre, the K'_{wc} , K'_{1c} , and K'_{2c} terms must be replaced with K'_w , K'_1 , and K'_2 , respectively.

PART III: WATER STABILIZATION DIAGRAMS

42. Stabilization involves adding certain chemicals to water to achieve a composition such that solid calcium carbonate will neither precipitate nor dissolve. Several chemicals may be used for this purpose, but only the most common, lime and carbon dioxide, are considered directly in this report.

Important Nomenclature

43. In the potable water supply industry, stabilization is usually accomplished by adding appropriate chemicals just before the water enters the distribution system. In the typical case where corrosion control is also an objective, the chemical doses are selected to produce a slightly supersaturated water. As this water flows through the distribution system calcium carbonate precipitates very slowly and deposits on interior surfaces, thus providing some corrosion protection. If conditions are such that enough time is provided, calcium carbonate will (in theory) precipitate until exact saturation (stability) is attained. This is, however, unlikely in actual practice because the precipitation reaction is so slow that the water is often removed from the distribution system before exact saturation can occur. A second factor is that other chemical activity occurring in the distribution system, for example the corrosion process itself, may affect carbonate stability dramatically. Nevertheless, it is quite useful to think of water in some "initial" (i.e. unstable) state being treated by the addition of lime and/or carbon dioxide and, hence, flowing through a distribution system where precipitation occurs until the "final" (i.e. stable) state is achieved. Furthermore, it is convenient to define a somewhat hypothetical "interim" state to represent the quality of the water immediately after lime and/or carbon dioxide are added, but before any precipitation of calcium carbonate takes place. In the following discussion the terms "initial," "interim," and "final" are used in this context.

Stabilization Criteria

44. The question of exactly what constitutes a well stabilized water is open to some debate. However, the following criteria, which are applicable to

the interim water, are generally accepted (Merrill and Sanks 1977):

Alkalinity	≥ 40 mg/l as CaCO_3
Calcium hardness	≥ 40 mg/l as CaCO_3
Calcium carbonate precipitation potential	4 to 10 mg/l as CaCO_3
pH	≤ 9.2 , but not between 8.0 and 8.5
Alkalinity	\approx calcium hardness, both expressed as mg/l as CaCO_3
Alkalinity	$\geq 5 \times$ (chloride + sulfate), all expressed as mg/l as CaCO_3

The water stabilization diagrams presented in Appendix A were constructed such that their use ensures that the first four criteria are automatically met, except that the interim pH is allowed to take on a value between 8 and 8.5. This exception is discussed in some detail below.

45. The reason for avoiding the pH 8 to 8.5 range is that, for a given water, buffer capacity is lowest within this region. From a practical point of view, this means that the ability of the water to resist a change in pH induced by the addition or removal of either acidic or basic constituents is lower in this pH range than at higher or lower pH. This is important because chemical and biochemical reactions (e.g., the corrosion process, or oxidation of iron by chemoautotrophic bacteria) occurring in water distribution systems may tend to alter the pH of the water. If the water has insufficient capacity to resist, the pH may change enough to significantly affect the carbonate system. This can result in an initially stable water becoming unstable and either promoting corrosion, or depositing excessive amounts of calcium carbonate scale.

46. However, the buffer capacity of a water is a function of both alkalinity and pH. Thus, a water having an alkalinity of, for example, 200 mg/l as CaCO_3 will, for a given pH, have a greater buffer capacity than a water having an alkalinity of, for example, only 50 mg/l as CaCO_3 . This clearly indicates that a criterion related to a minimum acceptable buffer capacity is what is needed. Simply avoiding an arbitrary pH range, such as that from 8.0 to 8.5, is not a rational approach. Unfortunately, no method for estimating a minimum acceptable buffer capacity has been developed. The diagrams presented in Appendix A were, therefore, not designed to automatically avoid the pH 8.0 to 8.5 region. Rather, they were designed to provide a warning whenever this situation arises, and let the user decide if the potential problem merits further action.

47. The requirement that pH be less than 9.2 is a rational one. Higher levels of pH can result in undesirable allergic reactions in a significant fraction of the population. Additionally, magnesium hydroxide will tend to precipitate in water heaters and hot water lines if the magnesium concentration exceeds about 40 mg/l as CaCO_3 and pH is greater than about 9.2. Thus, this criterion provides an adequate margin of safety for most waters of interest.

48. The requirement that alkalinity and calcium hardness be approximately equal is sound from an equilibrium chemistry point of view. However, rigid adherence to this criterion often involves excessive expense for stabilization. It is believed by the authors that keeping both the minimum alkalinity and calcium hardness above 40 mg/l as CaCO_3 is almost always sufficient, and the extra chemical requirement for making them roughly equal is unwarranted, except in very rare cases.

49. The criterion relating to the relationship between alkalinity and the sum of the chloride and sulfate concentrations is important for unlined iron or steel pipe only. Since the occurrence of excessive concentrations of chloride and sulfate is relatively rare, and only two types of pipe are affected, this requirement has been ignored for this study.

50. Finally, it is widely recommended that the calcium carbonate precipitation potential be in the 4- to 10-mg/l as CaCO_3 range. Higher values may be associated with excessive precipitation and, hence, increased flow resistance and clogging, while lower values indicate insufficient protection from corrosion. For this study, a precipitation potential of 4 mg/l as CaCO_3 was chosen as a target precipitate. This is sufficient for protection, avoids excessive precipitation, and simplifies the stabilization diagrams considerably.

Development of Stabilization Diagrams

Basic assumptions and relationships

51. Consider a water that has been treated with sufficient lime and/or carbon dioxide to precipitate a certain quantity of calcium carbonate and has done so until exact saturation (stability) has been achieved. For this water, the final state may be described by the following relationships.

$$ALKF = ALK + LA - PRE \quad (46)$$

$$CAF = CA + LA - PRE \quad (47)$$

$$ACDF = ACD - LA + CO_2A \quad (48)$$

where

ALKF, ALK = initial and final alkalinity of the water, respectively

LA, CO_2A = quantities of lime and carbon dioxide added to the water, respectively

PRE = quantity of calcium carbonate precipitated as the quality of the water changes from the initial to the final state

CAF, CA = initial and final calcium hardness of the water, respectively,

ACDF, ACD = initial and final acidity of the water, respectively

Furthermore, the hypothetical interim state can be represented as follows:

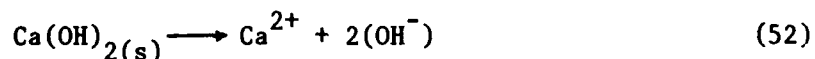
$$ALKI = ALK + LA \quad (49)$$

$$CAI = CA + LA \quad (50)$$

$$ACDI = ACD - LA + CO_2A \quad (51)$$

where ALKI, CAI, and ACDI = the interim alkalinity, calcium hardness, and acidity, respectively. All the terms in Equations 46 through 51 must be expressed in directly comparable units, for example, equivalents per litre or milligrams per litre as $CaCO_3$. For convenience, the latter means of expression is used in the remainder of this development. A brief explanation of the logic and assumptions underlying Equations 46 through 51 is presented below.

52. For the purposes of this development, assume that any lime added to a water dissolves instantly and completely. Thus, using hydrated lime as an example, we can write the following expression:



That is, each mole of lime added produces one mole of calcium ion and two moles of hydroxyl ion. Since there are two equivalents of lime and calcium

ion per mole, but only one equivalent of hydroxyl ion per mole, each equivalent of lime produces one equivalent of both calcium and hydroxyl ions. Or, using other units of expression, each milligram per litre as CaCO_3 of lime added produces 1 mg/l as CaCO_3 of both calcium and hydroxyl ions.

53. Recalling Equations 34 and 35,

$$(\text{ALK}) = (\text{CO}_3^{2-}) + (\text{HCO}_3^-) + (\text{OH}^-) - (\text{H}^+) \quad (34)$$

$$(\text{ACD}) = (\text{H}_2\text{CO}_3) + (\text{HCO}_3^-) + (\text{H}^+) - (\text{OH}^-) \quad (35)$$

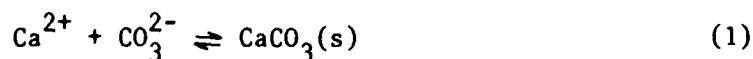
we see that, because hydroxyl ions are produced when the lime dissolves, alkalinity is increased and acidity is decreased in direct proportion to the amount of lime added. Since calcium ions are also produced in direct proportion to the amount of lime that dissolves, it is obvious, by definition, that the calcium hardness must also increase directly with lime addition.

54. By recalling Equations 13 and 14,



and remembering that it is virtually impossible to distinguish between dissolved carbon dioxide and carbonic acid, it is clear from Equation 35 that the addition of carbon dioxide increases acidity directly and by an amount equal to the amount of carbon dioxide added. However, the addition of carbon dioxide has no effect on either alkalinity or calcium hardness so long as solid calcium carbonate does not dissolve.

55. Precipitation and dissolution of calcium carbonate was earlier represented by Equation 1 as



It is evident from this expression that if a certain amount, PRE, of calcium carbonate precipitates, calcium hardness must decrease by an equal amount. Consideration of Equations 1 and 34 together reveals that precipitation of calcium carbonate reduces alkalinity by an amount equal to that precipitated

because carbonate ions are removed from solution. However, precipitation of calcium carbonate does not affect acidity. Thus, from the foregoing discussion, it is clear that Equations 46 through 51 are merely mass balance expressions based on simple chemical stoichiometry.

56. From the practical viewpoint of a water treatment plant operator, much of the foregoing discussion would appear to be of only academic value. However, the equations developed above may be used as described below to construct simple charts that operators may use to select the chemical doses required to stabilize virtually any water they are likely to encounter. The means by which these charts, called "Water Stabilization Diagrams," may be constructed is presented below.

Rationale for diagram construction

57. In describing the development of the water stabilization diagrams presented in Appendix A, it is convenient to begin at the final (stable) state of a water and look backward at how the water came to be in that state. Therefore, consider a water having initial alkalinity ALK and calcium hardness CA that has been treated with a certain quantity LA of lime and a certain quantity CO₂A of carbon dioxide to achieve slight supersaturation, and that has subsequently precipitated a certain amount PRE of calcium carbonate so that exact saturation has been attained. For this water we may rewrite Equation 34 as

$$ALKF = HCO_3F + CO_3F + OHF - HF \quad (53)$$

where

ALKF = alkalinity at the final state

HCO₃F = bicarbonate ion concentration at the final state

CO₃F = carbonate ion concentration at the final state

OHF = hydroxyl ion concentration at the final state

HF = hydrogen ion concentration at the final state

As was the case for Equation 34, directly comparable units must be used.

58. We may also combine Equations 29 and 33 to develop the following expression

$$HCO_3F = \frac{(CO_3F)(HF)}{K'_{2c}} \quad (54)$$

Equations 17 and 23 may be similarly combined to yield

$$\text{OHF} = \frac{K'_{wc}}{\text{HF}} \quad (55)$$

Substituting Equations 54 and 55 into Equation 53 we have

$$\text{ALKF} = \frac{(\text{CO}_3\text{F})(\text{HF})}{K'_{2c}} + \text{CO}_3\text{F} + \frac{K'_{wc}}{\text{HF}} - \text{HF} \quad (56)$$

59. Since the final state is, by definition, an exactly saturated one, we may combine Equations 2 and 12 to yield

$$\text{CO}_3\text{F} = \frac{K'_{sc}}{\text{CAF}} \quad (57)$$

Substituting Equation 57 into Equation 56 we have

$$\text{ALKF} = \frac{(K'_{sc})(\text{HF})}{(K'_{2c})(\text{CAF})} + \frac{K'_{sc}}{\text{CAF}} + \frac{K'_{wc}}{\text{HF}} - \text{HF} \quad (58)$$

This expression indicates that, for a water that is exactly saturated with calcium carbonate, there is a functional relationship between alkalinity and hydrogen ion concentration (which is, in turn, a function of pH). If the initial alkalinity and calcium hardness, and the amounts of lime and carbon dioxide added, are known, the only unknown in Equation 58 is the final hydrogen ion concentration HF.

60. Equation 58 may be solved with the aid of the quadratic formula to yield

$$\text{HF} = \frac{\frac{K'_{2c}[(\text{ALKF})(\text{CAF}) - K'_{sc}]}{K'_{sc} - (K'_{2c})(\text{CAF})} \pm \left(\left\{ \frac{K'_{2c}[(\text{ALKF})(\text{CAF}) - K'_{sc}]}{K'_{sc} - (K'_{2c})(\text{CAF})} \right\}^2 - \frac{(4)(K'_{wc})(K'_{2c})(\text{CAF})}{K'_{sc} - (K'_{2c})(\text{CAF})} \right)^{1/2}}{2} \quad (59)$$

Both the positive and negative roots will yield theoretically possible solutions. However, for well conditioned, potable waters, the positive root should always be used. Once the final hydrogen ion concentration is known, the final pH may be determined as shown below:

$$\text{pH F} = -\log \left[\frac{(\text{HF})(G_M)}{50,000} \right] \quad (60)$$

61. Since the final alkalinity and hydrogen ion concentration are known, the final acidity may be determined by rewriting Equation 45 for the final state as follows:

$$ACDF = \frac{\left(ALKF \frac{K'_{wc}}{HF} + HF\right)\left(1 + \frac{HF}{K'_{1c}}\right)}{1 + \frac{K'_{2c}}{HF}} - \frac{K'_{wc}}{HF} + HF \quad (61)$$

62. Knowing the final acidity, and the amounts of lime and carbon dioxide added to achieve stabilization, the initial acidity may be determined from mass balance considerations. That is, Equation 48 may be rewritten as

$$ACD = ACDF + LA - CO_2A \quad (62)$$

Then, since both the initial acidity and alkalinity are known, the correct values can be substituted into Equation 45 to yield an expression in which the initial hydrogen ion concentration H is the only unknown:

$$ACD = \frac{\left(ALK - \frac{K'_{wc}}{H} + H\right)\left(1 + \frac{H}{K'_{1c}}\right)}{1 + \frac{K'_{2c}}{H}} - \frac{K'_{wc}}{H} + H \quad (63)$$

Unfortunately, this expression is of the fourth order with respect to H , and an exact analytical solution is not possible. If high speed computing facilities are available, it is possible to simply substitute the known value of ALK and an assumed value of H into Equation 63, calculate the corresponding value of ACD , and compare it to the known value. Then, depending upon the results of the comparison, assume a new value of H and repeat the process until the predicted and known values of ACD agree to the desired level of accuracy. Other solution techniques are also available.

63. If calculations must be made by hand, it is best to simplify Equation 63 by dropping the appropriate terms. For example, for values of pH greater than about 6, the H terms may be ignored with little loss of accuracy and, for values of pH less than about 9, the K'_{wc}/H terms need not be considered. Thus, for the pH range of about 6 to 9, a simplified form of Equation 63 may be solved directly for H using the quadratic formula. Similarly,

for pH values greater than about 9, the H/K'_{ic} term is rather insignificant and can be ignored. Again, a direct solution of a modified version of Equation 63 may be obtained with the aid of the quadratic formula. In the pH range right around 9, either approximate solution will be exact enough for most purposes.

64. Once the initial hydrogen ion concentration is determined, the initial pH may be calculated from

$$pH = -\log \left[\frac{(H)(G_M)}{50,000} \right] \quad (64)$$

65. The alkalinity ALKI and acidity ACDI of the interim water may be determined from simple mass balance considerations presented earlier:

$$ALKI = ALK + LA \quad (49)$$

$$ACDI = ACD - LA + CO_2A \quad (51)$$

Once these values are known, they can be substituted into Equation 45 (rewritten for the interim state) to yield an expression for the interim hydrogen ion concentration HI. This expression may be solved by either the iterative or approximate methods described above. The interim pH can then be determined from

$$pHI = -\log \left[\frac{(HI)(G_M)}{50,000} \right] \quad (65)$$

Generating a diagram

66. The "backwards" approach described above may be used to generate the water stabilization diagrams mentioned earlier. To illustrate the approach, assume that a certain water is described as shown below:

Temperature	25° C
Total dissolved solids	400 mg/l
Alkalinity	100 mg/l as CaCO ₃
Calcium hardness	40 mg/l as CaCO ₃

It is desired to treat this water in such a manner that the hypothetical interim water meets the criteria for a well conditioned water discussed earlier. That is,

Alkalinity	≥ 40 mg/l as CaCO_3
Calcium hardness	≥ 40 mg/l as CaCO_3
pH	≤ 9.2
Calcium carbonate precipitation potential	4 mg/l as CaCO_3

A water stabilization diagram for this water may be developed as follows.

67. First, assume that it is necessary to add 55 mg/l of lime (as CaCO_3) and no carbon dioxide to stabilize this water. Thus, from Equations 46 and 47 we may write

$$\text{ALKF} = 100 + 55 - 4 = 151 \text{ mg/l as } \text{CaCO}_3$$

$$\text{CAF} = 40 + 55 - 4 = 91 \text{ mg/l as } \text{CaCO}_3$$

Substituting these values into Equation 59 yields

$$\text{HF} = 8.906 \times 10^{-4} \text{ mg/l as } \text{CaCO}_3$$

$$\text{pH F} = 7.79$$

68. Then, substituting the correct values of ALKF and HF into Equation 61 reveals that

$$\text{ACDF} = 159.83 \text{ mg/l as } \text{CaCO}_3$$

Since the final acidity is now known, the initial acidity can be determined from Equation 62 as

$$\text{ACD} = 159.83 + 55 - 0 = 214.83$$

This value, along with the initial alkalinity (100 mg/l), can be substituted into Equation 63, which can be solved by the iterative procedure to yield

$$\text{H} = 1.520 \times 10^{-2} \text{ mg/l as } \text{CaCO}_3$$

and, from Equation 64,

$$\text{pH} = 6.56$$

69. The interim alkalinity, calcium hardness, and acidity may be calculated using Equations 49, 50, and 51, respectively, as

$$\text{ALKI} = 100 + 55 = 155 \text{ mg/l as CaCO}_3$$

$$\text{CAI} = 40 + 55 = 95 \text{ mg/l as CaCO}_3$$

$$\text{ACDI} = 214.83 - 55 + 0 = 159.83 \text{ mg/l as CaCO}_3$$

70. Finally, the interim hydrogen ion concentration and pH may be determined from Equations 45 (rewritten for the interim condition) and 65, respectively, as shown below:

$$\text{HI} = 5.785 \times 10^{-4} \text{ mg/l as CaCO}_3$$

$$\text{pHI} = -\log \frac{(5.785 \times 10^{-4})(0.902)}{50,000} = 7.98$$

71. Since

$$\text{pHI} < 9.2,$$

$$\text{ALKI} > 40 \text{ mg/l as CaCO}_3,$$

$$\text{CAI} > 40 \text{ mg/l as CaCO}_3,$$

the interim water meets the specified criteria. Thus, if the initial pH of the water is 6.56, 55 mg/l of lime (expressed as CaCO_3) must be added to achieve the desired interim state. This pair of values ($\text{LA} = 55$, $\text{pH} = 6.56$) represents a single point on the curve shown on the left side of Figure 1. By selecting a new lime dose (e.g., 50 mg/l as CaCO_3) and repeating the entire procedure, a second point ($\text{LA} = 50$, $\text{pH} = 6.61$) can be identified. If this process is continued until $\text{LA} = 0$, the entire curve shown on the left side of Figure 1 can be plotted.

72. This curve can be used to determine the amount of lime needed to stabilize any water having an alkalinity of 100 mg/l, calcium hardness of 40 mg/l, and initial pH between 6.56 and 8.74, so long as 25°C and 400 mg/l

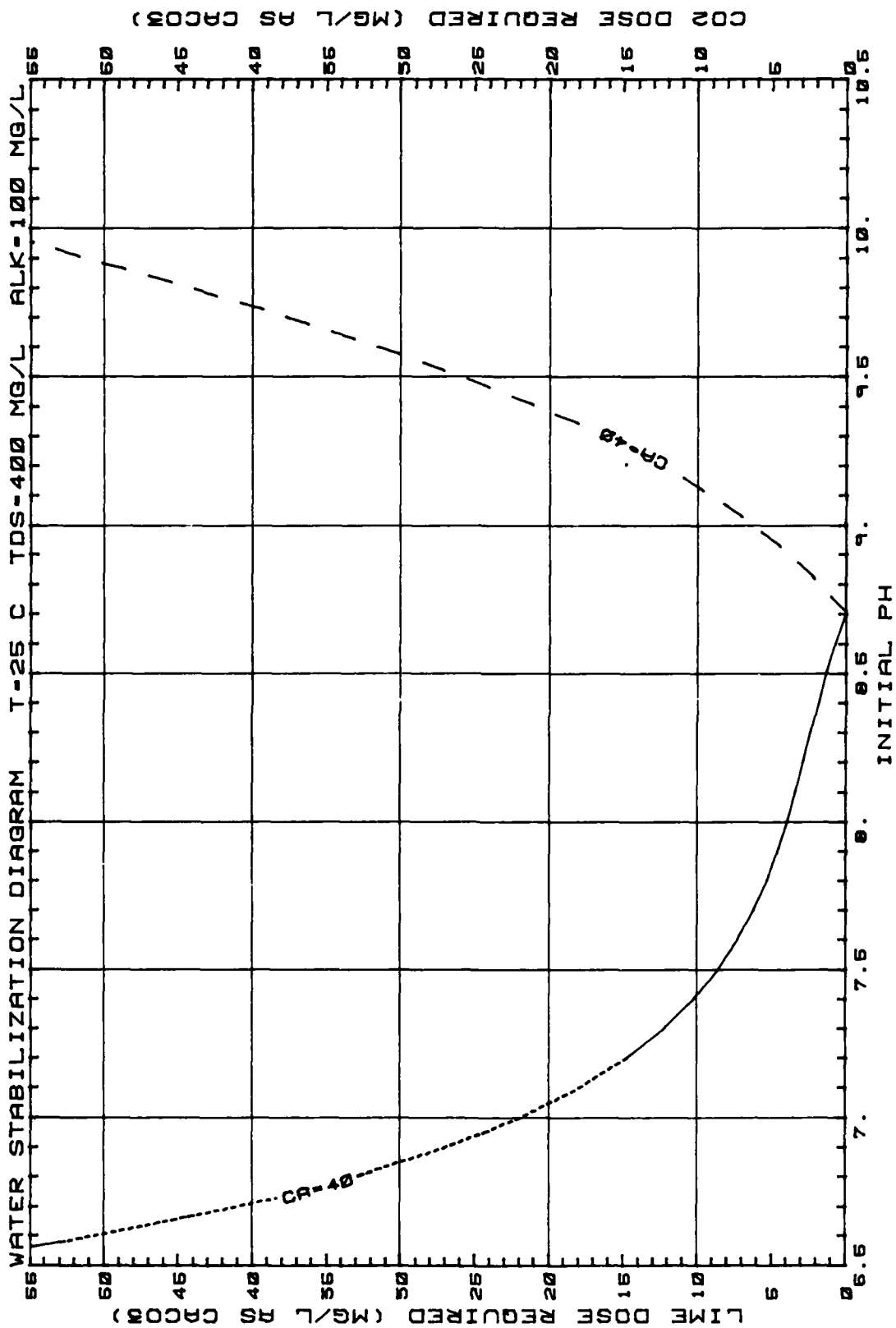


Figure 1. Example of single curve on water stabilization diagram

are reasonable approximations of the water temperature and total dissolved solids concentrations, respectively. The maximum lime dose plotted, 55 mg/l as CaCO_3 , has no particular significance, except that it is sufficient for most practical problems and allows for a convenient scale of 10 mg/l to the inch.

73. After the line representing the relationship between the initial pH and the amount of lime needed to achieve stabilization has been fully defined, the curve on the right side of Figure 1 may be constructed. This is done by assuming a zero lime dose and letting the required carbon dioxide dose vary from zero to the maximum value that can conveniently be plotted (55 mg/l as CaCO_3 in this case). A procedure similar to that described above for constructing the line on the left half of the figure can be used. The result is a curve that shows the relationship between initial pH and the carbon dioxide dose required for stabilization, for the pH range of 8.74 to 9.95. For convenience, the carbon dioxide curve is shown by dashed lines while a solid and/or dotted line is used for the lime dose required. Again for convenience, the left ordinate is labeled in terms of lime and the right ordinate is labeled in terms of carbon dioxide. However, since the scales and units of expression are exactly the same, either ordinate may be used with either curve. The abscissa is scaled so that one inch is equal to one pH unit.

74. Taken as a whole, Figure 1 may be used over the entire pH range of 6.56 to 9.95 to determine the amounts of lime or carbon dioxide needed to stabilize the water having the characteristics previously described. This range is inclusive enough to cover the vast majority of cases likely to be encountered in practice. However, different curves will be needed for other waters. Families of curves that may be used to determine the chemical doses required for waters having an alkalinity of 100 mg/l as CaCO_3 , temperatures and total dissolved solids concentration reasonably close to 25° C and 400 mg/l, respectively, and calcium hardness varying from 300 to 40, and 40 to 1 mg/l as CaCO_3 are shown in Figures 2 and 3, respectively.

Interpretation of Diagrams

75. It is of interest to consider the chemical interpretation of the curves shown in Figure 1 in some detail. For example, if the pH is approximately 8.69, no chemical addition is required. Waters having a lower pH are undersaturated, or insufficiently supersaturated, and, therefore, lime is

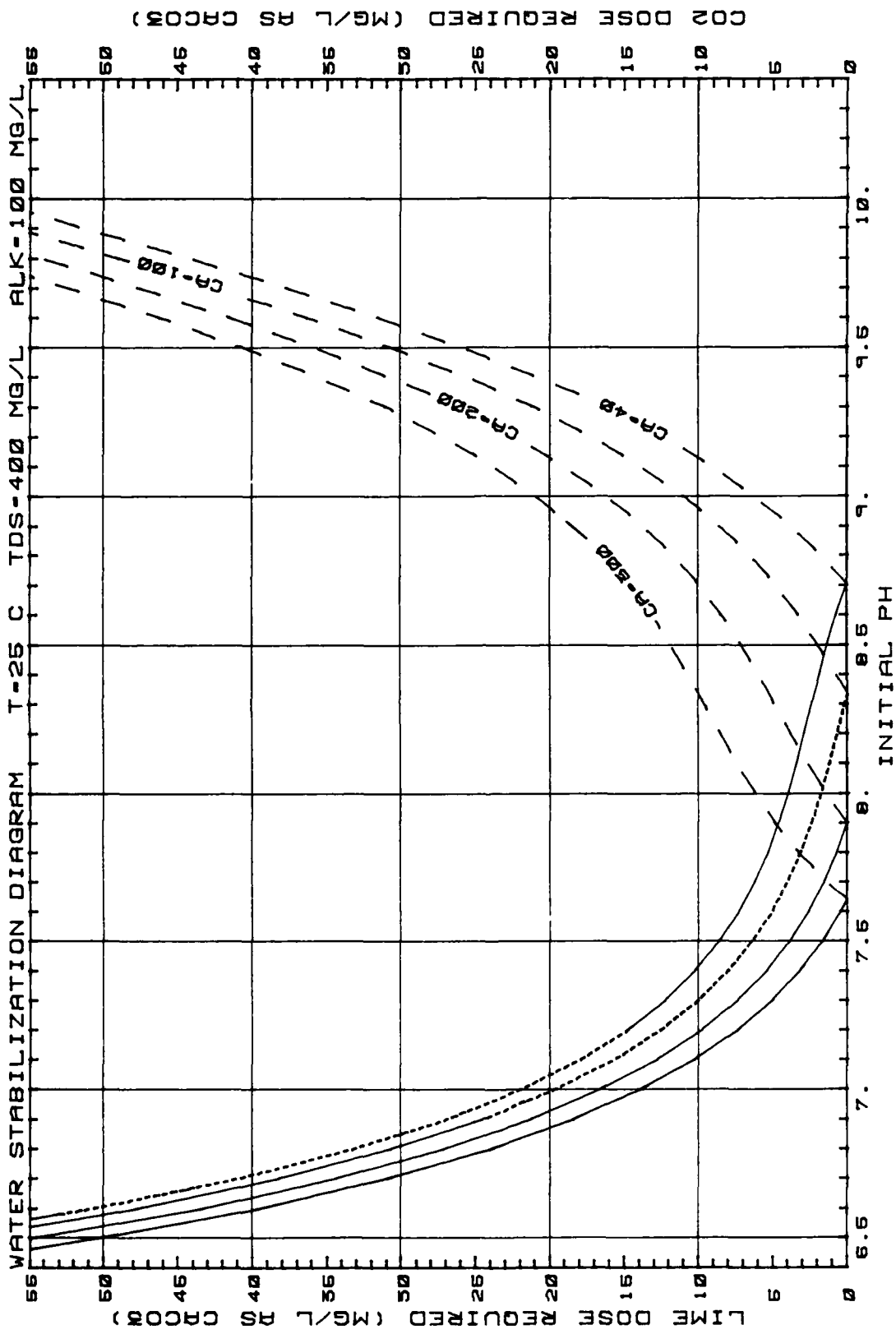


Figure 2. Example of water stabilization diagram (high Ca)

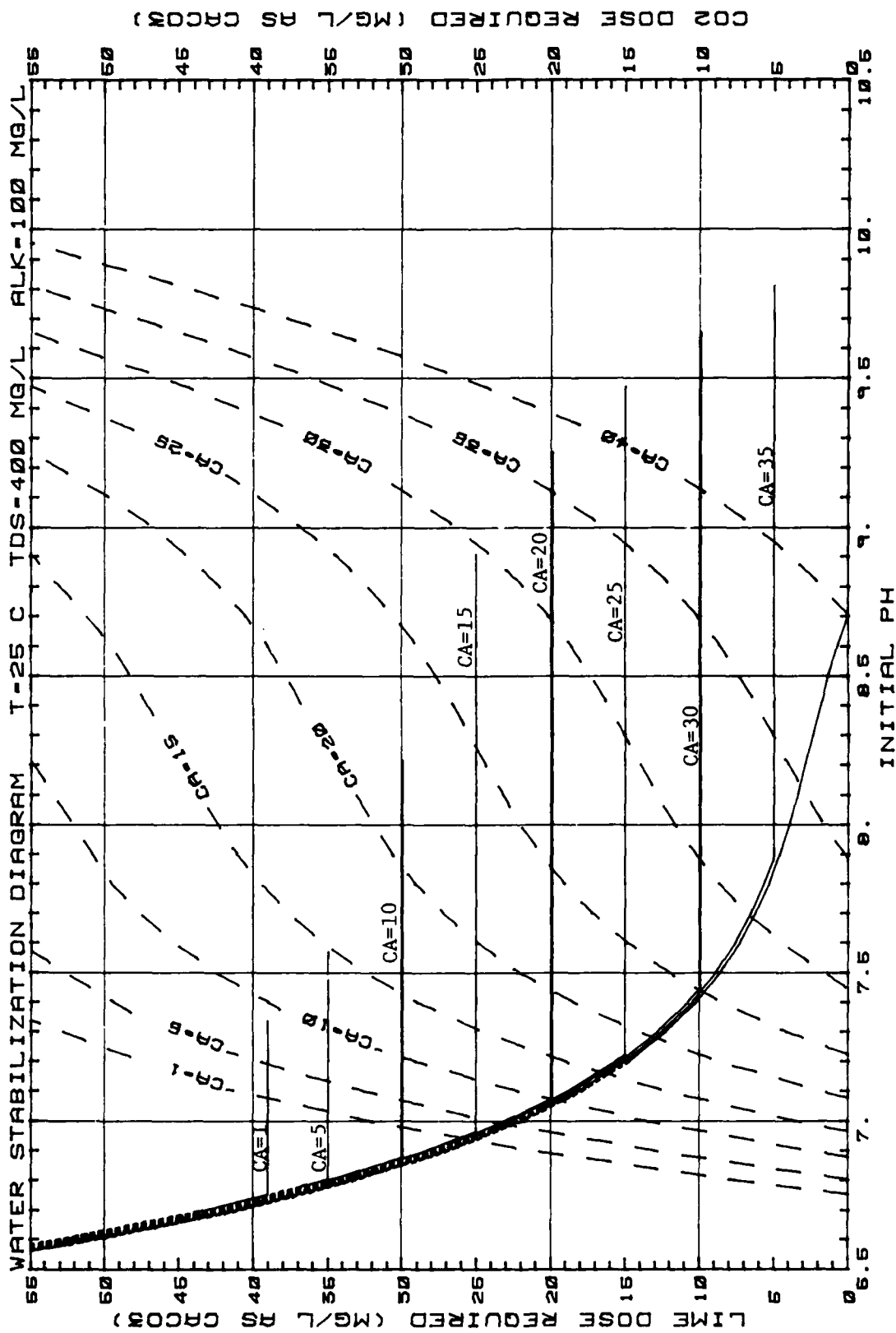


Figure 3. Example of water stabilization diagram (low Ca)

needed to raise the pH, alkalinity, and hardness to achieve the desired 4-mg/l precipitation potential. Waters having a higher pH are excessively supersaturated and will tend to form more precipitate than is desired. Thus, pH must be lowered by adding carbon dioxide until a 4-mg/l precipitation potential is attained.

76. Even a casual observer would notice that, in Figure 1, the curve showing the relationship between initial pH and the lime dose required is composed of both dotted and solid segments. The significance of the dotted segment is that, for the region of the curve, the interim pH falls within the 8.0 to 8.5 (i.e. low buffer capacity) range. This may, or may not, be important in a particular case, but serves as a convenient method of warning the user of possible problems.

77. Inspection of Figure 3 reveals that not all the plotted lines intersect the abscissa. For example, consider the curves for calcium hardness equal to 25 mg/l as CaCO_3 . The lime curve begins at 55 mg/l (initial pH about 6.6) and continues downward and to the right until the lime dose is 15 mg/l (initial pH about 7.2) and then proceeds horizontally at the 15-mg/l value. This is because a minimum of 15 mg/l of lime must be added to satisfy the 40-mg/l minimum interim calcium hardness criteria ($40 - 25 = 15$). For waters having pH greater than 7.22, both lime and carbon dioxide must be added. Thus, the carbon dioxide curve begins along the abscissa, at the point where pH is equal to about 7.2, and proceeds upward and to the right to the maximum dose shown (55 mg/l at a pH of 9.47). The curves take on a similar shape when the interim pH reaches the allowable maximum value of 9.2. For these cases, both lime and carbon dioxide must be added to produce water having the desired interim quality.

Interpolating for Intermediate Values

Calcium hardness and alkalinity

78. When the calcium hardness of a water to be stabilized falls between curves plotted on the appropriate diagram, linear interpolation may be used to obtain sufficiently accurate estimates of the required chemical doses. This can be confirmed by inspection of Figure 3. For example, the curves for a calcium hardness of 20 mg/l as CaCO_3 lie approximately midway between those for 15 and 25 mg/l. Thus, interpolation between adjacent curves for chemical doses corresponding to intermediate values of calcium hardness is feasible.

It is also possible to interpolate between adjacent diagrams (i.e. between alkalinity values) when a diagram is not available for the exact alkalinity of the water to be stabilized. This is illustrated by Figure 4 which was constructed for 25° C, 400 mg/l total dissolved solids, 40 mg/l as CaCO_3 calcium hardness, and alkalinities of 160, 180, and 200 mg/l as CaCO_3 . As may be seen, even though the curves do intersect, the curves for an alkalinity of 180 mg/l as CaCO_3 fall roughly midway between the curves for alkalinities of 160 and 200 mg/l as CaCO_3 . Thus, again, linear interpolation for chemical doses corresponding to intermediate alkalinities is shown to be a reasonable approach. The specific alkalinity values chosen to construct the diagrams presented in Appendix A were selected so as to facilitate interpolation for intermediate values.

Total dissolved solids

79. It is also of interest to consider the effects of varying total dissolved solids concentrations (i.e. varying ionic strength). While the absolute magnitude of this effect will vary for different waters, the relative impact is relatively small. This is illustrated by Figure 5 which shows curves for 25° C, 100 mg/l as CaCO_3 alkalinity, 40 mg/l as CaCO_3 calcium hardness, and total dissolved solids concentrations of 40, 400, and 1200 mg/l. As may be seen, the effect of the total dissolved solids concentration on the required chemical dose is relatively small. Therefore, there is no need to interpolate for intermediate values. Rather, it is sufficient to simply choose the diagram for the total dissolved solids concentration closest to the actual value and proceed directly.

Temperature

80. The effect of temperature is somewhat more pronounced than that of total dissolved solids. This is illustrated by Figure 6 which shows curves for 400 mg/l total dissolved solids, 100 mg/l as CaCO_3 alkalinity, 40 mg/l as CaCO_3 calcium hardness, and temperatures of 5°, 15°, and 25° C. Clearly there is a considerable temperature effect. However, it may not be necessary to interpolate for intermediate temperatures. Merrill and Sanks (1977) in discussing a similar problem associated with the use of Caldwell-Lawrence diagrams suggested that reasonable answers can be obtained from diagrams constructed for conditions (i.e., total dissolved solids and temperature) not greatly different from those of the water being considered. If a more exact solution is desired, linear interpolation may be used with reasonable results.

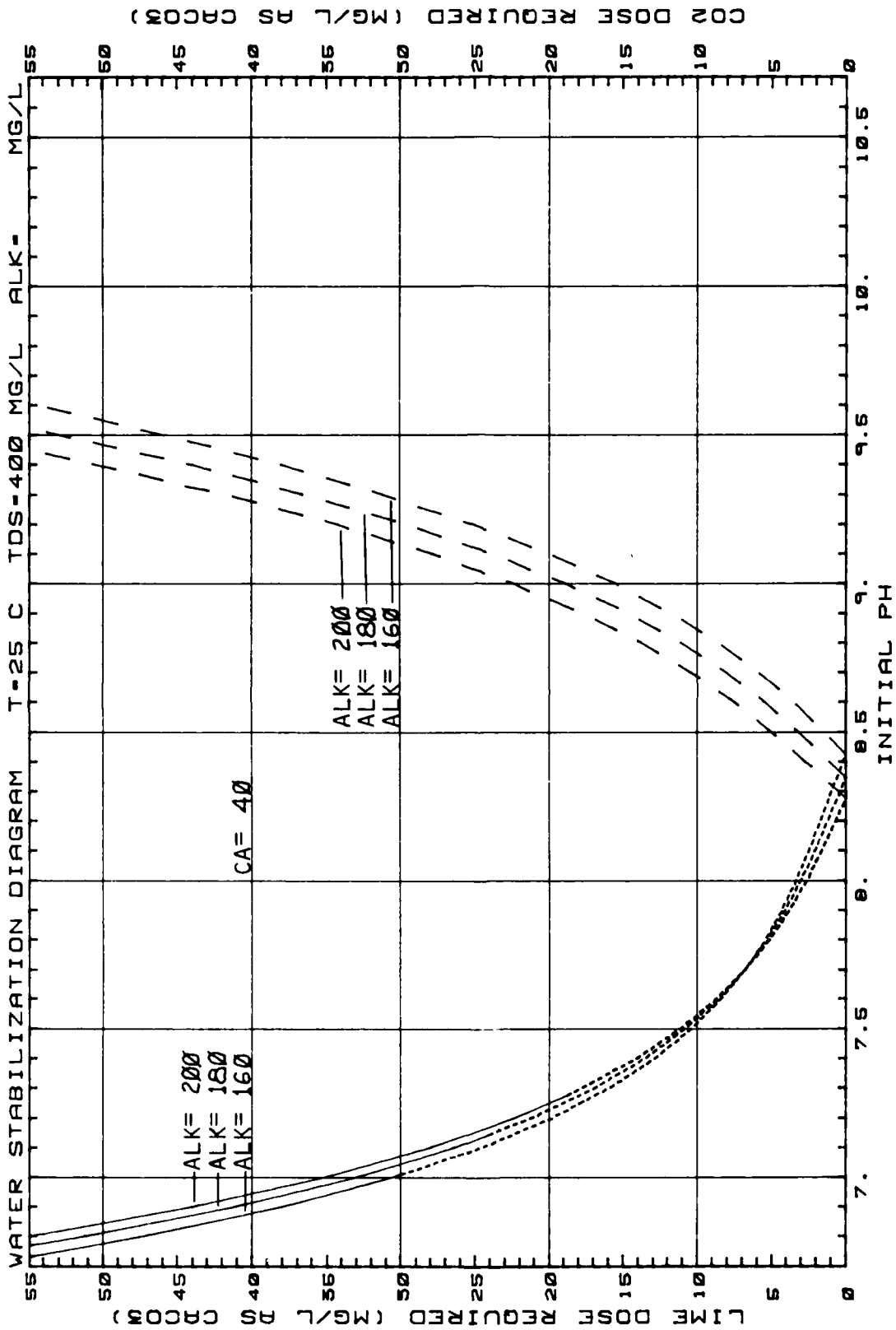


Figure 4. Effect of varying alkalinity

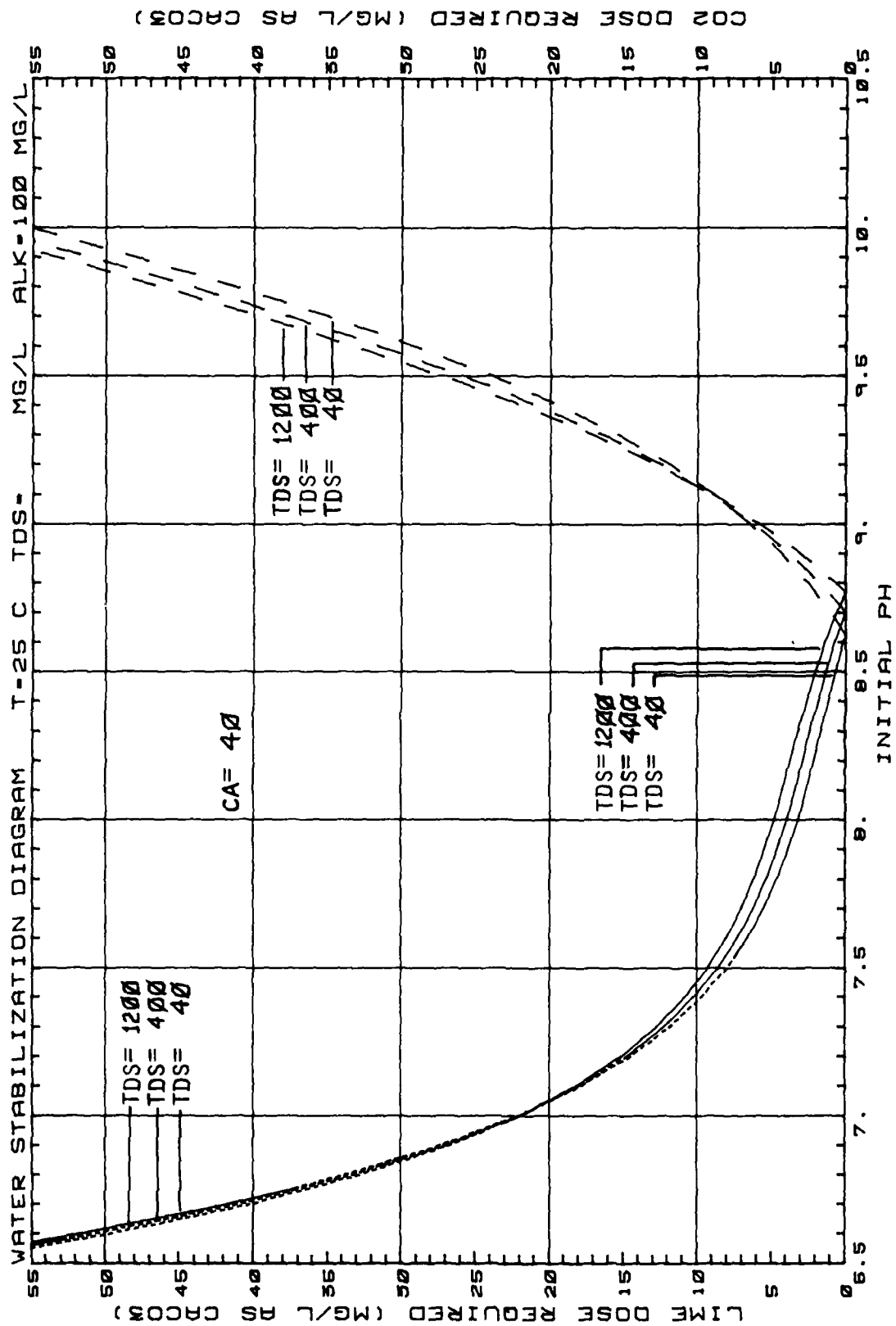


Figure 5. Effect of varying total dissolved solids (ionic strength)

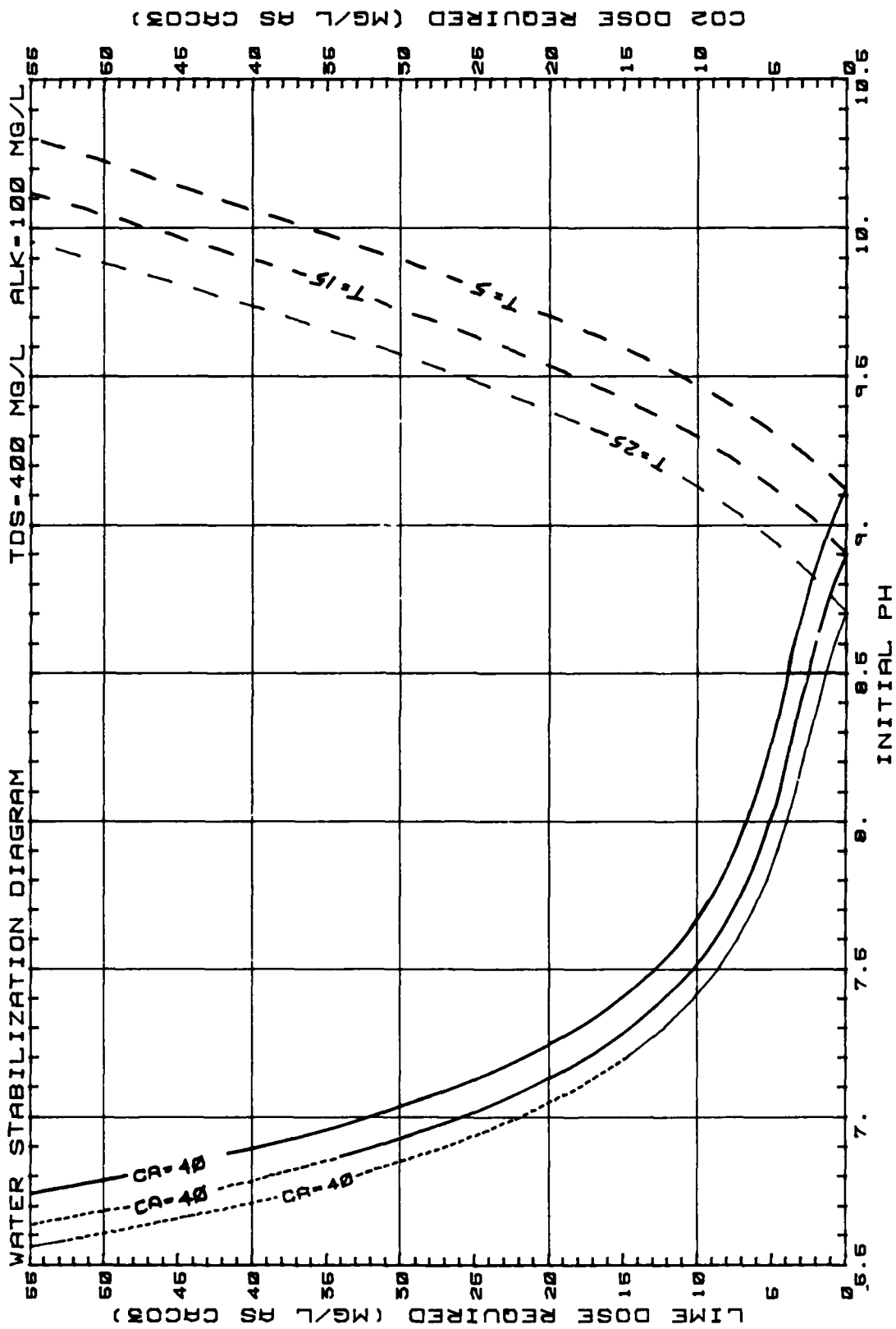


Figure 6. Effect of varying temperature

PART IV: EXAMPLE APPLICATIONS

Introduction

81. The water stabilization diagrams presented in Appendix A of this report may be used directly to determine the doses of lime and carbon dioxide required to stabilize virtually all waters of interest to the potable water supply industry, subject to the criteria described below. Specifically, the diagrams have been designed to ensure that the interim water (i.e. water that has been treated to achieve stability, but which has yet to begin to precipitate any calcium carbonate) will have the following characteristics:

Alkalinity	≥ 40 mg/l as CaCO_3
Calcium hardness	≥ 40 mg/l as CaCO_3
pH	≤ 9.2
Precipitation potential	4 mg/l as CaCO_3

82. The microcomputer program described in Part V is somewhat more flexible in that the user may specify the precipitation potential desired. In addition, the microcomputer program expresses the chemical dose requirements as milligrams per litre as CaCO_3 , milligrams per litre as Ca(OH)_2 , milligrams per litre as CaO , or milligrams per litre as CO_2 , as appropriate; and informs the user of the interim pH, and the final alkalinity, calcium hardness, and pH of the stabilized water. At the option of the user, the microcomputer program can also express the chemical doses required in terms of milligrams per litre and pounds per hour of commercially available product.

83. In either case (i.e. the diagrams or the microcomputer program), the following must be known about the water to be treated:

Temperature, °C
Total dissolved solids, mg/l
Alkalinity, mg/l as CaCO_3
Calcium hardness, mg/l as CaCO_3
pH

Example applications of the diagrams to solve typical water stabilization problems are presented below. However, before looking at the examples, the reader should turn to Appendix A and read the introductory material presented there.

Examples

Example 1

84. A water to be stabilized has the following characteristics:

Total dissolved solids	40 mg/l
Temperature	15° C
Alkalinity	80 mg/l
Calcium hardness	20 mg/l
pH	8.1

Find the quantities of lime and carbon dioxide required to stabilize this water.

85. The first step in solving this problem is to locate the proper diagram by referring to Table A1. As can be seen, diagram A15 is exactly suited to this problem. For convenience, this diagram has been reproduced as Figure 7.

86. To determine the lime dose required, enter the diagram at pH 8.1 and read vertically upward to the solid line labeled CA = 20 (i.e. calcium hardness = 20 mg/l as CaCO_3). Then, read horizontally to the vertical LIME DOSE REQUIRED axis (left-hand axis). The lime dose required may be read directly as 20 mg/l as CaCO_3 .

87. To determine the carbon dioxide dose required, enter the diagram at pH 8.1 and read vertically upward to the dashed line labeled CA = 20 (i.e., calcium hardness = 20 mg/l as CaCO_3). Then, read horizontally to the vertical CO_2 DOSE REQUIRED axis (right-hand axis). The carbon dioxide dose required may be read directly as 32.5 mg/l as CaCO_3 .

Example 2

88. Find the lime and carbon dioxide doses needed to stabilize a water having the characteristics shown below:

Total dissolved solids	40 mg/l
Temperature	15° C
Alkalinity	80 mg/l
Calcium hardness	22 mg/l
pH	8.1

89. Obviously, this problem is almost the same as Example 1 and can be

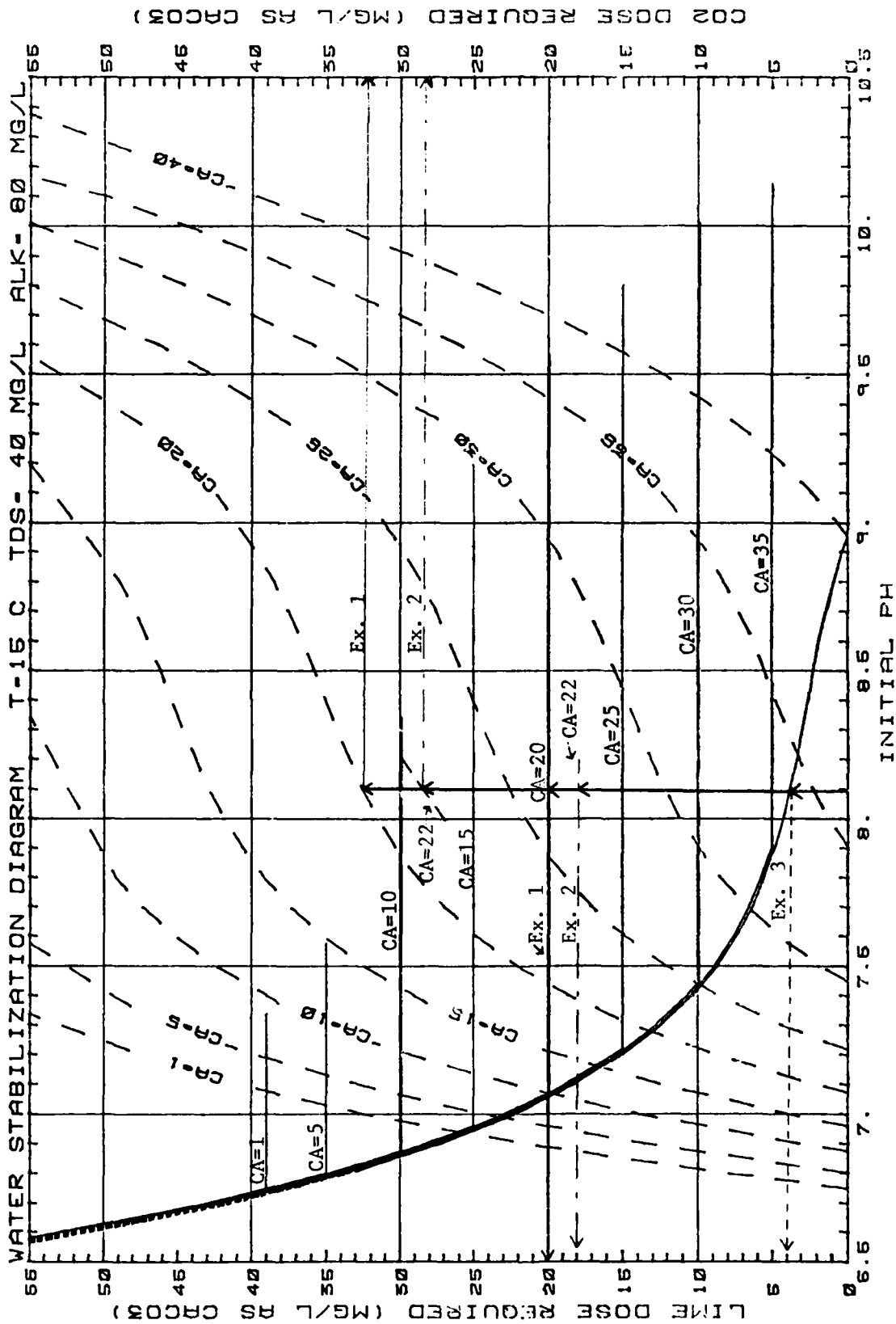


Figure 7. Water stabilization diagram for Examples 1, 2, and 3

worked using the same diagram (A15, or Figure 7). However, there are no lines for 22 mg/l calcium hardness. Thus, the user must interpolate to obtain an answer. The simplest approach is to "eyeball" the locations of the CA = 22 curves and proceed as in Example 1. This method (shown in Figure 7) indicates that the required lime and carbon dioxide doses are 18 and 28.5 mg/l as CaCO₃, respectively.

90. An alternative is to solve the problem for CA = 20 and CA = 25 and interpolate for the final answers. This method is illustrated below:

Calcium Hardness mg/l as CaCO ₃	Lime Dose mg/l as CaCO ₃	CO ₂ Dose mg/l as CaCO ₃
20	20	32.5
22	?	?
25	15	22.5

For CA = 20 we may use linear interpolation as follows:

$$\text{Lime Dose} = 15 + \left(\frac{25 - 22}{25 - 20} \right) (20 - 15) = 15 + 3 = 18 \text{ mg/l as CaCO}_3$$

$$\text{CO}_2 \text{ Dose} = 22.5 + \left(\frac{25 - 22}{25 - 20} \right) (32.5 - 22.5) = 22.5 + 6 = 28.5 \text{ mg/l as CaCO}_3$$

As indicated, the methods produce the same results. With a bit of practice, most users will find the "eyeball" approach both easy to use and sufficiently precise for virtually all practical problems.

Example 3

91. Find the lime and carbon dioxide doses required to stabilize the following water:

Total dissolved solids	40 mg/l
Temperature	15° C
Alkalinity	80 mg/l as CaCO ₃
Calcium hardness	40 mg/l as CaCO ₃
pH	8.1

Again, diagram A15 (Figure 7) is appropriate.

92. Reading vertically upward at pH 8.1 to the solid CA = 40 line and, hence, horizontally to the LIME REQUIRED axis indicates that the required lime dose is 4 mg/l as CaCO₃. However, reading vertically upward at pH 8.1

reveals that there is no intersection with the dashed $CA = 40$ line. Since there is no intersection, the required carbon dioxide dose is zero. That is, no carbon dioxide is required to stabilize this water.

Example 4

93. Find the lime and carbon dioxide doses required to stabilize the following water:

Total dissolved solids	40 mg/l
Temperature	25° C
Alkalinity	45 mg/l as $CaCO_3$
Calcium hardness	24 mg/l as $CaCO_3$
pH	8.6

94. Inspection of Table A1 reveals that there is no diagram exactly suited to this problem. However, there are two diagrams, A63 and A65, that bracket the given water. That is, both diagrams are suitable as far as total dissolved solids and temperature are concerned, but the alkalinity specified (45 mg/l as $CaCO_3$) falls in between the values of 40 (A63) and 60 (A65) mg/l for which the diagrams were constructed. Thus, to solve this problem, we must interpolate between two diagrams. Furthermore, since there are no $CA = 24$ lines, we must interpolate (or use the eyeball technique) for the calcium hardness values as well.

95. First, solve the problem assuming an alkalinity of 40 mg/l as $CaCO_3$ (i.e. using diagram A63, reproduced here as Figure 8). Using the eyeball method for $CA = 24$, note (see Figure 9) that the required lime and carbon dioxide doses are 16 and 27 mg/l, respectively. Similarly, from the diagram for an alkalinity of 60 mg/l (A64, reproduced here as Figure 9) we see that the required lime and carbon dioxide doses are 16 and 28 mg/l, respectively.

96. To obtain final answers, interpolate between the results obtained from the diagrams, that is,

Alkalinity mg/l as $CaCO_3$	Lime Dose mg/l as $CaCO_3$	CO_2 Dose mg/l as $CaCO_3$
40	16	27
45	?	?
60	16	28

97. Since the lime dose required is the same for both the 40- and

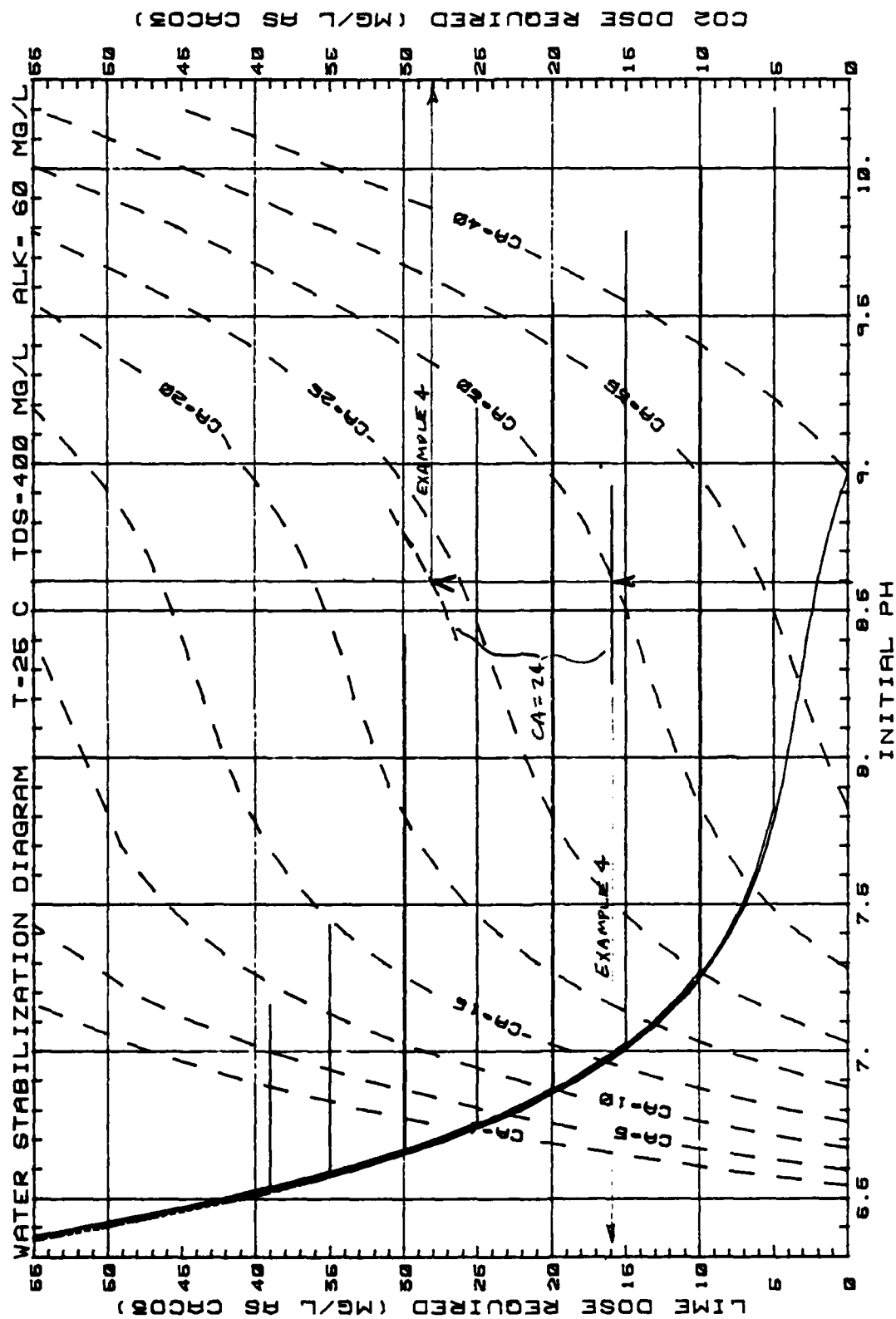


Figure 9. Water stabilization diagram for Example 4 (alkalinity = 60 mg/l)

60-mg/l alkalinity diagrams, it is obvious that the lime dose required for this case, alkalinity of 45 mg/l, is also 16 mg/l as CaCO_3 . The reason this is the case is that the lime dose required for this case is controlled by the requirement that the interim calcium hardness must be ≥ 40 mg/l as CaCO_3 (i.e. $40 - 24 = 16$). In the general case this will not be true and linear interpolation would have to be used to determine the required lime dose.

98. The required carbon dioxide dose may be calculated as

$$\text{CO}_2 \text{ Dose} = 27 + \left(\frac{45 - 40}{60 - 40} \right) (28 - 27) = 27 + 0.25 = 27.25 \text{ mg/l as } \text{CaCO}_3$$

However, for most purposes there would be no need to actually perform this calculation as one could simply use the 27-mg/l value. This illustrates the fact that considerable care was used in selecting the diagrams presented in Appendix A so that, for most cases, there will be no need for complicated interpolation calculations to determine the required chemical doses.

Example 5

99. So far the water temperatures specified in the examples have corresponded exactly to those for which diagrams are presented in Appendix A (5°, 10°, 15°, 20°, and 25° C). However, consider the following water:

Total dissolved solids	40 mg/l
Temperature	18° C
Alkalinity	80 mg/l as CaCO_3
Calcium hardness	200 mg/l as CaCO_3
pH	7.2

For this case, there is no exactly applicable diagram. However diagrams A50 and A68 "bracket" this water. That is, they are suitable with respect to total dissolved solids, alkalinity, calcium hardness, and pH, but diagram A50 is for 15° C while diagram A68 is for 25° C. There is no diagram for 18° C. Thus, we must solve the problem for the 15° and 25° C temperatures and interpolate for answers corresponding to the desired temperature, 18° C.

100. From diagram A50, reproduced here as Figure 10, for a temperature of 15° C the required lime and carbon dioxide doses are 11.8 and 0 mg/l, respectively. Similarly, from diagram A68, reproduced here as Figure 11, we see that for a temperature of 25° C the required lime and carbon dioxide doses are 9 and 0 mg/l, respectively.

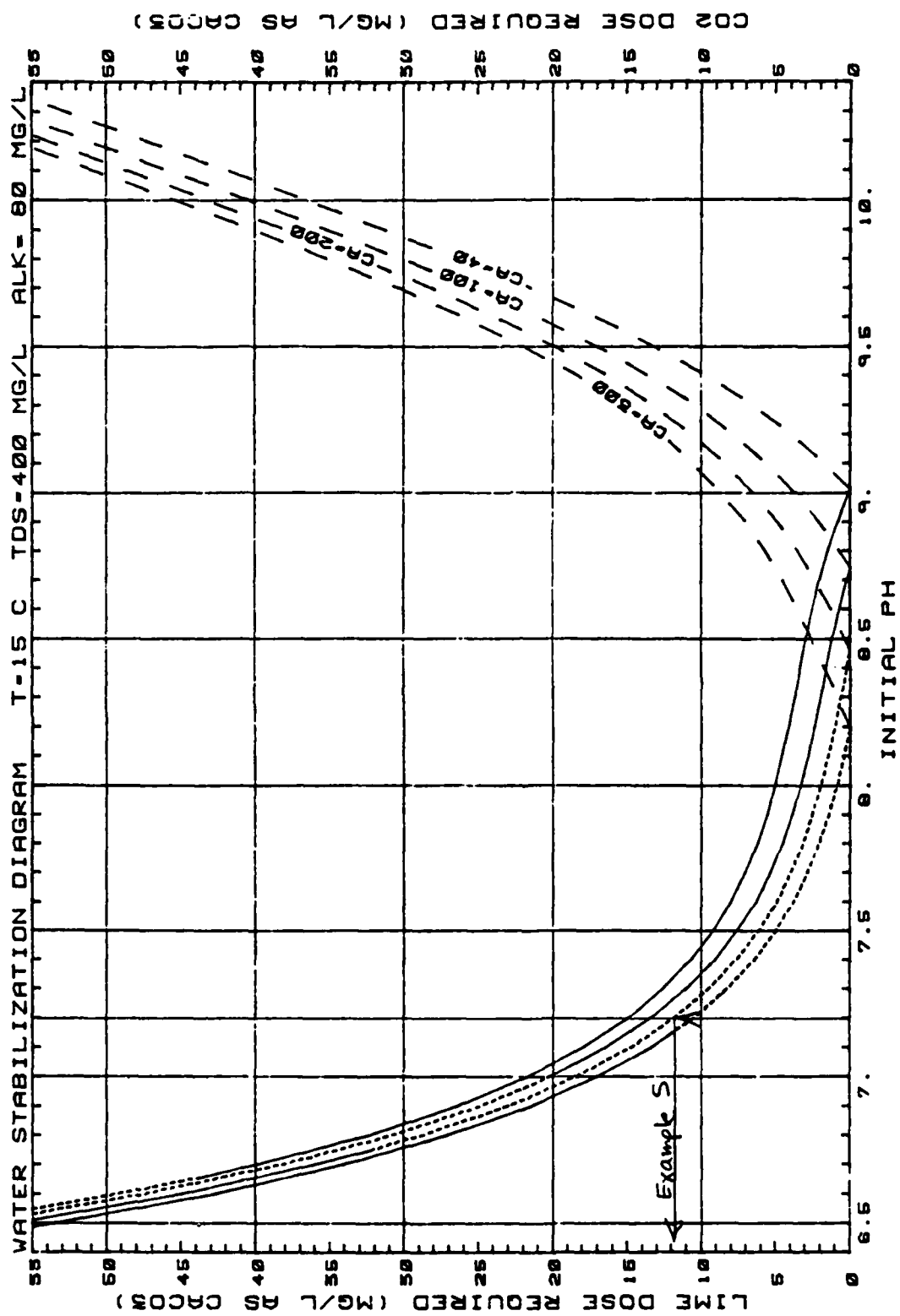


Figure 10. Water stabilization diagram for Example 5 (temperature = 15° C)

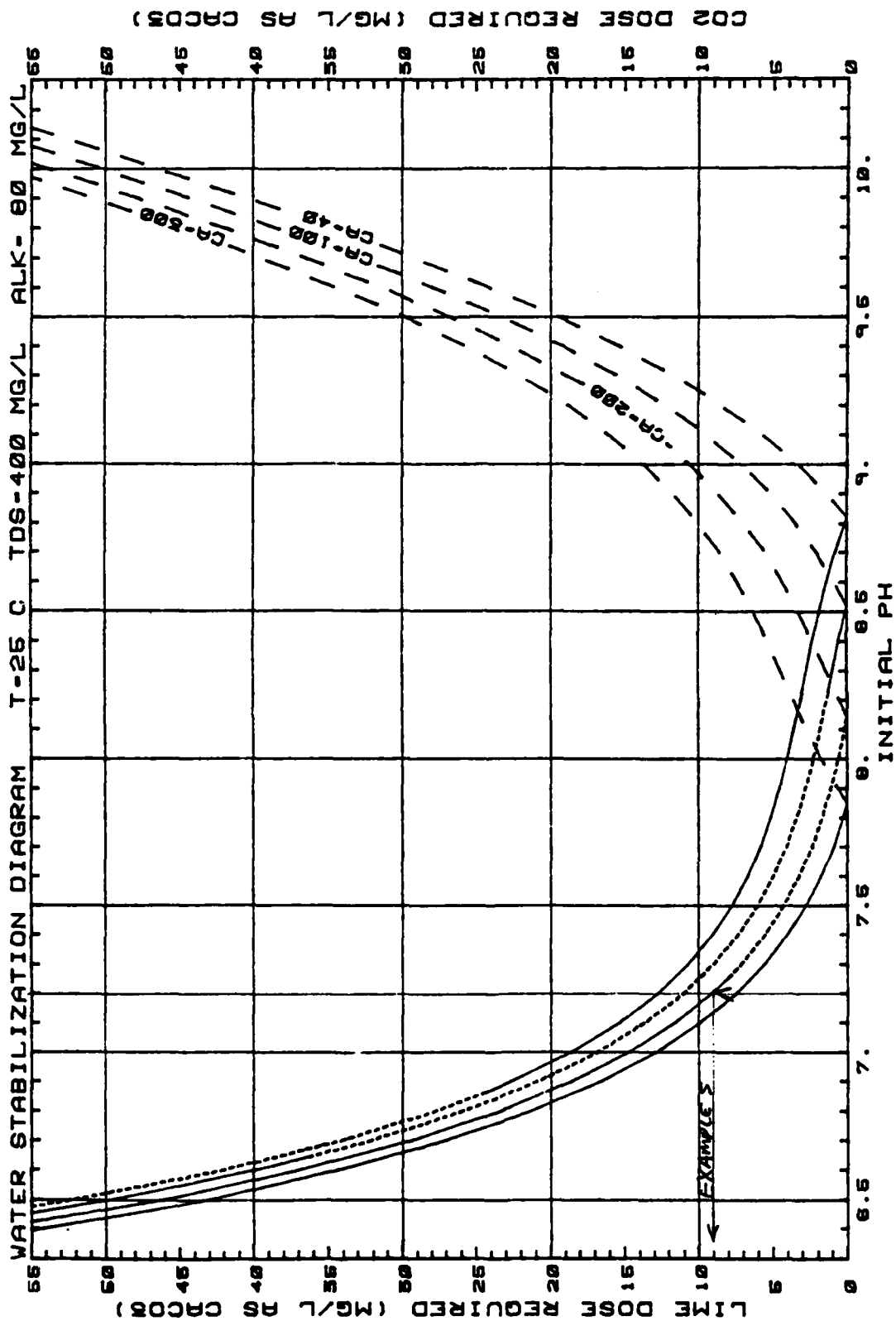


Figure 11. Water stabilization diagram for Example 5 (temperature = 25° C)

101. To obtain final answers we must again interpolate, that is:

Temperature °C	Lime Dose mg/l as CaCO_3	CO_2 Dose mg/l as CaCO_3
15	11.8	0
18	?	?
25	9.0	0

The required lime dose is

$$\text{Lime Dose} = 9 + \left(\frac{25 - 18}{25 - 15} \right) (11.8 - 9) = 9 + 1.96 = 10.96 \text{ mg/l as } \text{CaCO}_3$$

The required carbon dioxide dose is zero since it is zero for both 15° and 25° C.

102. Again this example illustrates that the diagrams presented in Appendix A were carefully selected to avoid having to interpolate over wide ranges. With practice, many users will develop the ability to estimate the required chemical doses with satisfactory precision without actually making any calculations on paper. For example, in this case we could easily have looked at the diagrams for 15° and 25° C and estimated the required lime dose to be 11 mg/l.

103. This example also emphasizes another feature of the diagrams. When solving the problem for 15° C (Figure 10) note that the CA = 200 line is dotted rather than solid at the pH of interest (i.e., 7.2). For the 25° C case, the line is solid at pH = 7.2, but is dotted in the near vicinity (pH 7.25). Therefore, in that initial pH range the interim pH will fall in the 8.0 to 8.5 range. As indicated in Parts II and III this may, or may not, be significant. Nevertheless, the diagrams do provide a warning of possible problems associated with low buffer capacity.

Example 6

104. Usually it is necessary to express the results obtained in Example 1 in terms of pounds per hour of commercially available calcium oxide (quicklime) and carbon dioxide for a 10-MGD (million gallon per day) treatment facility. To do this we must convert the answers from 20 mg/l as CaCO_3 for the lime dose, and 32.5 mg/l as CaCO_3 for the carbon dioxide dose, to the units of expression indicated above. Furthermore, assume that the quicklime available commercially is 90 percent pure and the carbon dioxide is 100 percent pure.

105. For the quicklime, we may write

$$\text{Quicklime Dose} = \left(20 \frac{\text{mg}}{\ell} \text{ as } \text{CaCO}_3\right)(0.56) = 11.2 \text{ mg}/\ell \text{ as CaO}$$

Then, to convert to milligrams per litre of commercial product, we may write

$$\text{Quicklime Dose} = \left(11.2 \frac{\text{mg}}{\ell}\right)\left(\frac{100}{90}\right) = 12.4 \text{ mg}/\ell \text{ as commercial lime}$$

To determine feed rate multiply by the flow and conversion factors

$$\text{Quicklime Dose} = \frac{\left(12.4 \frac{\text{mg}}{\ell}\right)(8.34)(10)}{24} = 43 \text{ lb/hr as commercial CaO}$$

The 0.56 term used to convert from milligrams per litre as CaCO_3 to milligrams per litre as CaO is simply the ratio of the equivalent weight of CaO to that of CaCO_3 (i.e., $28/50 = 0.56$). The 100/90 term used to convert from milligrams per litre as CaO to milligrams per litre as commercially available CaO is simply the ratio of 100 percent purity to the purity of the commercial product (i.e. 90 percent, in this case). The 8.34 term used to convert from milligrams per litre as commercial product to pounds per hour is a factor that converts milligrams per litre to pounds per million gallons. Dividing by 24 converts pounds per day to pounds per hour. The factor 10 is the flow rate in million gallons per day.

106. To summarize, we can use the following conversion factors:

<u>To Convert from</u>	<u>To</u>	<u>Multiply by</u>
mg/l as CaCO_3	mg/l as CaO*	0.56
mg/l as CaCO_3	mg/l as Ca(OH)_2 **	0.74
mg/l as CaCO_3	mg/l as CO_2	0.44
mg/l pure chemical	mg/l commercial product	100/percent purity of commercial product
mg/l commercial product	lb/hr commercial product	$(0.3475)(\text{flow rate in MGD})$ [0.3475 = 8.34 lb/gal/ 24 hr/day]

* CaO = quicklime.

** Ca(OH)_2 = hydrated (slaked) lime.

Using these rules, the amount of commercially available carbon dioxide required for the example is:

$$\text{CO}_2 \text{ Dose} = \frac{(32.5)(0.44)(100/100)(8.34)(10)}{24} = 50 \text{ lb/hr}$$

General Procedure

107. Based on the examples presented above, a general procedure to follow in solving stabilization problems is provided below:

- a. Look at Table A1 and select the proper diagram(s). This is done by first deciding which total dissolved solids concentration is applicable. To do this, choose either 40 mg/l, 400 mg/l, or 1200 mg/l, whichever is closer to the total dissolved solids of the water of interest. There is no need to interpolate for intermediate values of total dissolved solids as chemical dose is only slightly dependent on total dissolved solids.
- b. Then, within the total dissolved solids concentration chosen, select the set of diagrams for the temperature range (5°, 10°, 15°, 20°, or 25° C) corresponding most closely to the temperature of the water in question. If no set of diagrams is available for the exact temperature desired, select diagrams from both the next higher and next lower temperature sets.
- c. Next, within the set of diagrams selected, choose the diagram(s) for alkalinity corresponding most closely to that of the water in question. If no diagram(s) is available for the exact alkalinity desired, select diagrams for the next higher and next lower alkalinities.
- d. In some cases more than one diagram is available for a given total dissolved solids, temperature, and alkalinity combination. In such a case, choose the diagram(s) for the desired calcium hardness.
- e. At this point the needed diagram(s) will have been identified. The total will range from 1 to 4 depending upon the exact values of temperature and alkalinity of interest, and the desired precision (i.e. is interpolation between diagrams required?).
- f. Use the diagram(s) to determine the required chemical doses. In the "worst" case, this will require eyeballing, or interpolating for the correct calcium hardness lines, interpolating for alkalinity, and interpolating for temperature--in that order. With some practice, the need for making calculations while interpolating will diminish.
- g. Finally, convert the chemical dose in milligrams per litre as CaCO_3 to feed rate of commercial chemical in pounds per hour by multiplying or dividing by the appropriate factors given in paragraph 106 which account for treatment plant flow and chemical purity.

PART V: MICROCOMPUTER PROGRAM

Introduction

108. The graphical method described in the other parts of this report provides an easy-to-use approach for determining lime and carbon dioxide dosages to produce a well conditioned water. The diagrams are based on producing a water with a precipitation potential of 4 mg/l as CaCO_3 , for specific discrete values of total dissolved solids (ionic strength), temperature, calcium hardness, and alkalinity. There is no simple way to use the graphs to determine dosages to achieve a precipitation potential other than 4 mg/l, and some interpolation is required since temperature, dissolved solids, calcium hardness, and alkalinity concentrations will seldom be one of the values for which the diagrams are exact.

109. The graphical solution for chemical dose will generally be adequate, but, in some instances, an individual may want to obtain an exact solution for a specific combination of input parameters for which a graphical solution is not available. Manual solution of the equations describing the problem, even with the help of Caldwell-Lawrence diagrams, is fairly difficult. Use of a computer to solve the problem can greatly reduce the effort involved.

110. With the current growth in acceptance of microcomputers and the fact that many utilities will have microcomputers in the not too distant future, the authors developed a microcomputer program to determine chemical dose. The advantage of this approach is that it treats temperature, desired precipitate, dissolved solids, calcium hardness, and alkalinity as continuous variables. It also gives chemical doses corrected for purity and feed rates in pounds per hour. The primary disadvantage of the computerized approach is that it does require use of a computer and, for computers that will not run IBM or Apple Basic, some conversion work.* The program is written in the BASIC computer language which is a popular language for small computers. Unfortunately, there is no standard BASIC language and most computer manufacturer(s) support versions of BASIC which are different from other versions. Two versions of this program were prepared so that the program could be run

* Use of trade names does not constitute an endorsement of the product.

without any modification on the two most popular brands of computers available at the time: IBM and Apple. Converting the program to another machine requires an understanding of the differences in the language on that machine and the language on IBM and Apple.

111. Listings of both versions of the program are included in Appendices B and C. To obtain a copy of the program on floppy disc (diskette), an individual can indicate whether the IBM or Apple version is desired and send a 5-1/4-in., single sided, double density floppy disc to:

U. S. Army Engineer Waterways Experiment Station (WES)
ATTN: Thomas M. Walski/WESEE-R
Box 631
Vicksburg, Miss. 39180

112. The hardware required to run the program consists of: (a) a central processor (i.e. the computer itself), (b) a monitor (TV screen), and (c) a memory device (disc drive if program is furnished by WES although if program is typed manually a tape device is adequate). If the user wishes to have printed output, a printer is required as the program can optionally prepare hard copy output.

113. The program is a public domain program, and therefore is not copyrighted. The program may be copied without any royalty payments.

114. The program can be run in either interpretive or compiler BASIC. Most simple systems have only interpretive BASIC. Using interpretive BASIC, the program runs in several minutes. The program will run in less than 1 min in compiler BASIC so the user is encouraged to use compiler BASIC and execute the compiled version whenever possible.

115. The documentation of the microcomputer program is given in the next section. The input and output for the program are then described, followed by instructions on how to run the program using first the IBM and then the Apple version.

Program Documentation

Definition of variables

116. Formulations for the water conditioning program were developed in Part III. These formulations used three- and four-character variables which were translated to two-character variables in the water conditioning program.

The use of two-character variables will greatly enhance the portability of the program to other microcomputers. The tabulation below provides the list of original formulation variables and the microprogram variables.

<u>Variables from Part III</u>	<u>Micro Program Variables</u>	<u>Variables from Part III</u>	<u>Micro Program Variables</u>
ACD	AD	CA	CA
ALK	AL	LA	LA
CO ₂ A	CO	PRE	PR
CAF	CF	ALKF	AF
ACDF	AC	ALKI	AI
ACDI	CI	T	T
TDS	TD	IS	IS
G	G	G _M	GM
G _D	GD	pK ₁	P1
pK ₂	P2	pK _w	PW
pK _s	PS	K ₁	K1
K ₂	K2	K _w	KW
K _s	KS	K' _{1c}	C1
K' _{2c}	C2	K' _{wc}	CW
K' _{sc}	CS	HF	HF
H	H	pH	pH
pHI	PI		

The following is a list of the variables used in the IBM personal computer water conditioning program. With each variable is the statement number of the initial reference to the variable, the meaning of the variable, and the initial value of the variable (if it exists).

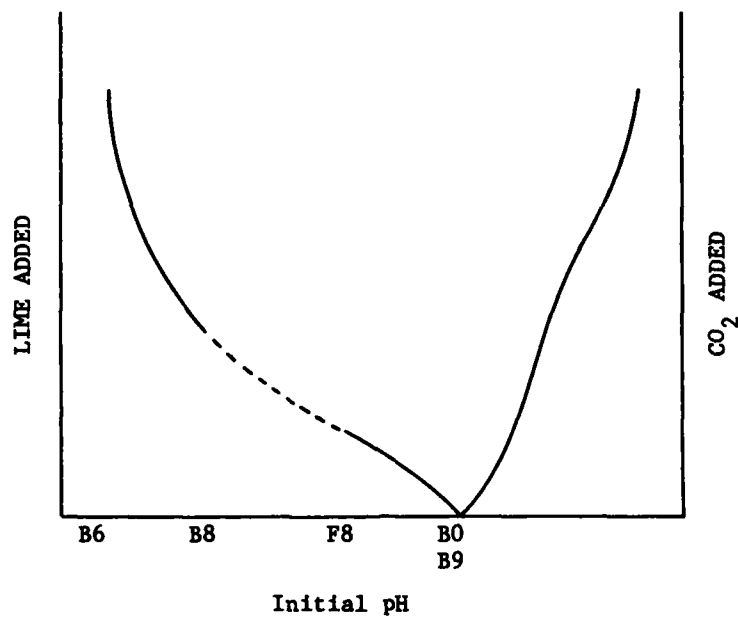
<u>Initial Reference</u>	<u>Variable Name</u>	<u>Definition</u>
40	V(20)	Return array for numeric values from free form routine
40	B\$(20)	Return array for alphanumeric words from free form routine
45	SS(4)	Save array for lime and CO ₂ output
275	KN	Indicator to proper subscript of save array
260	A\$	Input string
300	T	Temperature, °C
300	TD	Total dissolved solids, mg/l
300	PR	Desired precipitate, mg/l as CaCO ₃
310	AL	Alkalinity, mg/l as CaCO ₃
310	CA	Calcium, mg/l as CaCO ₃
310	VA	Initial pH
500	IS	Ionic strength as function of TD
510	A	Constant as function of T

(Continued)

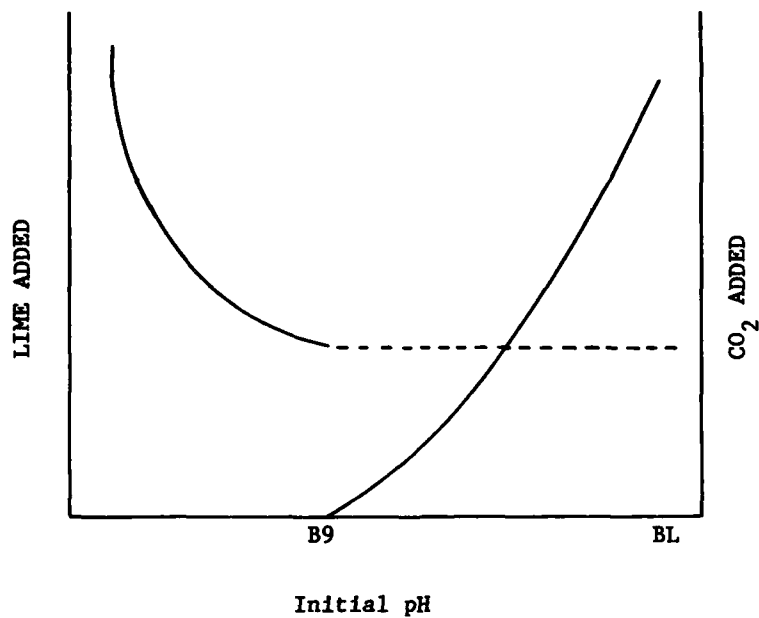
Initial Reference	Variable Name	Definition
520	G	Activity coefficient
530	GM	Activity coefficient for monovalent ions
530	GD	Activity coefficient for divalent ions
580	P1	Equilibrium constant as function of T
590	P2	Equilibrium constant as function of T
600	PW	Equilibrium constant as function of T
610	PS	Equilibrium constant as function of T
620	K1	Equilibrium constant as function of P1
630	K2	Equilibrium constant as function of P2
640	KW	Equilibrium constant as function of PW
650	KS	Equilibrium constant as function of PS
660	C1	Corrected equilibrium constants for ionic strengths, temperature, and the appropriate activity coefficient
670	C2	
680	CW	
690	CS	
800	LA	Lime added, mg/l as CaCO_3
800	CO	Carbon dioxide added, mg/l as CaCO_3
800	B6	Initial pH for LA = 101 and CO = 0 mg/l
800	I6	Interim pH for LA = 101 and CO = 0 mg/l
800	B0	Initial pH for LA = 0 and CO = 0 mg/l
800	I0	Interim pH for LA = 0 and CO = 0 mg/l
830	B8	Initial pH for interim pH = 8.0
840	F8	Initial pH for interim pH = 8.5
850	B9	Initial pH for interim pH = 9.2
860	BL	Maximum pH
860	CL	CO_2 added for maximum pH (BL) maximum of 101 mg/l CaCO_3
980	VS	Saved current value of pH
2040	LP	Purity of lime, percent
2050	CP	Purity of carbon dioxide, percent
2060	QA	Flow rate, MGD
2080	C\$	Output format string for lime added
2085	D\$	Output format string for CO_2 added

Variables such as B6 and F8 denote specific initial pH values corresponding to, for example, very high lime dose (101 mg/l) or interim pH of 8.0. These values are shown graphically in Figure 12. Several other variables are only used in the Apple version. They are given below:

Initial Reference	Variable Name	Definition
45	QS(4)	Feed rates, lb/hr
50	P\$	Input string for printer status
1990	LQ	Dose of quicklime, mg/l as CaO
1990	LH	Dose of hydrated lime, mg/l as Ca(OH)_2
2008	CX	Dose of carbon dioxide, mg/l as CO_2



a. Typical relationship between chemical dose and pH



b. Relationship between chemical dose and pH when minimum lime dose is required

Figure 12. Definition of initial pH values corresponding to specific chemical doses and interim pH ranges

Program logic

117. The steps used by the program to determine lime dose are listed below:

- Step 1: Display of title screen.
- Step 2: Input initial water condition data.
- Step 3: Equilibrium coefficients are calculated.
- Step 4: Significant pH limits are calculated.
 - a. For lime added = 101 and CO_2 added = 0, GOSUB 1210 to find B6.
 - b. For an interim pH = 8, GOSUB 1570 to find B8.
 - c. For an interim pH = 8.5, GOSUB 1570 to find F8.
 - d. For lime added = 0 and CO_2 added = 0, GOSUB 1210 to find B0.
 - e. If the interim pH at B0 > 9.2, then set interim pH = 9.2 and GOSUB 1570 to find B9. Otherwise, B9 = B0.
 - f. Set the initial pH = B9, GOSUB 1480 to find lime added at upper pH limit. Next, GOSUB 1740 to find upper pH limit BL at CO_2 added = 101.
 - g. Print allowable pH range.
- Step 5: Input the desired initial pH.
- Step 6: The lime added or CO_2 required for the specified precipitate is calculated.
 - a. If the initial calcium (CA) < 40.0, then set lime added = 40 - CA and CA and GOSUB 1660 to find CO_2 required. If the interim pH < 9.2, print results and go to Step 7. Otherwise go to Step 6b.
 - b. If the initial pH < B8, then set CO_2 added = 0 and GOSUB 1480 to find lime added. Print results and go to Step 7.
 - c. If B8 < initial pH < F8, then set CO_2 added = 0 and GOSUB 1480 to find lime added. Print results. ²As an alternate solution, GOSUB 1480 to find lime added for an initial pH = B8, then GOSUB 1660 to find CO_2 added for the desired initial pH. Print results and go to Step 7.
 - d. If F8 < initial pH < B9, then set CO_2 added = 0 and GOSUB 1480 to find lime added. Print results and go to Step 7.
 - e. If the initial pH > B9, then set CO_2 added = 0, GOSUB 1480 to find lime added at initial pH = B9, and GOSUB 1660 to find CO_2 added for the desired initial pH. Print results and go to Step 7.
- Step 7: Input chemical purities and flow rate or start new problem Step 2.
- Step 8: Chemical feed rates are calculated.

Step 9: Print feed rates.

Step 10: If desired, repeat from Step 2, otherwise end program.

Subroutine calls and logic

118. For each subroutine (GOSUB) call, the initial statement of the subroutine, purpose of the subroutine, line numbers that reference the subroutine, and a variable list of the subroutine and subroutine logic are provided below.

Initial Statement 1210

Purpose: Calculate the initial pH and interim pH for given LA (lime added) and CO (carbon dioxide added) dosages

Referenced from line numbers 800 870 1530 1620 1690 1760

Reference	Name	Definition
1230	CF	Final Ca^{++} concentration, mg/l as CaCO_3
1240	AF	Final alkalinity, mg/l as CaCO_3
1250	RA	Radical in calculation of final pH
1260	HF	Final hydrogen concentration
1265	PH	Final pH
1270	AC	Final acidity, mg/l as CaCO_3
1310	AD	Initial acidity, mg/l as CaCO_3
1350	AI	Sum of alkalinity and lime added, mg/l as CaCO_3
1350	CI	Final acidity, mg/l as CaCO_3
1420	PI	Interim pH
Return	1430	

The logic for Subroutine 1210 is shown below:

Calculate:	Final calcium	CF
	Final alkalinity	AF
	Final H ion concentration	HF
	Final pH	PF
	Final acidity	AC
	Initial acidity	AD

GOSUB 1780

Calculate H ion concentration corresponding to the desired initial acidity

<RETURN>

Calculate:	Initial pH	PH
	Interim alkalinity	AI
	Interim acidity	CI

GOSUB 1880

Calculate H ion concentration corresponding to the desired interim acidity

<RETURN>

Calculate:	Interim pH	PI
	<RETURN>	

Initial Statement 1480

Purpose: Calculate the LA (lime added) dosage required to produce a desired initial pH with CO (carbon dioxide added) dosage constant

Referenced from line numbers 860 960 980 1010 1040 1050

<u>Reference</u>	<u>Name</u>	<u>Definition</u>
1500	NC	Increment of LA (lime added); initial value = 10.0
1530	PH	Initial pH produced by the LA and CO
1530	VA	Desired initial pH
Return	1540	

Subroutine logic is shown in Figure 13.

Initial Statement 1570

Purpose: Calculate the LA (lime added) dosage required to produce a desired interim pH with the CO (carbon dioxide added) dosage constant

Referenced from line numbers 830 840 850

<u>Reference</u>	<u>Name</u>	<u>Definition</u>
1590	NC	Increment of LA (lime added); initial value = 10.0
1590	LA	Lime added to produce the desired interim pH; initial value = 101 mg/l
1620	PI	Interim pH produced by the LA and CO
1620	VA	Desired interim pH
Return	1630	

The logic for this subroutine is the same as that for subroutine 1480.

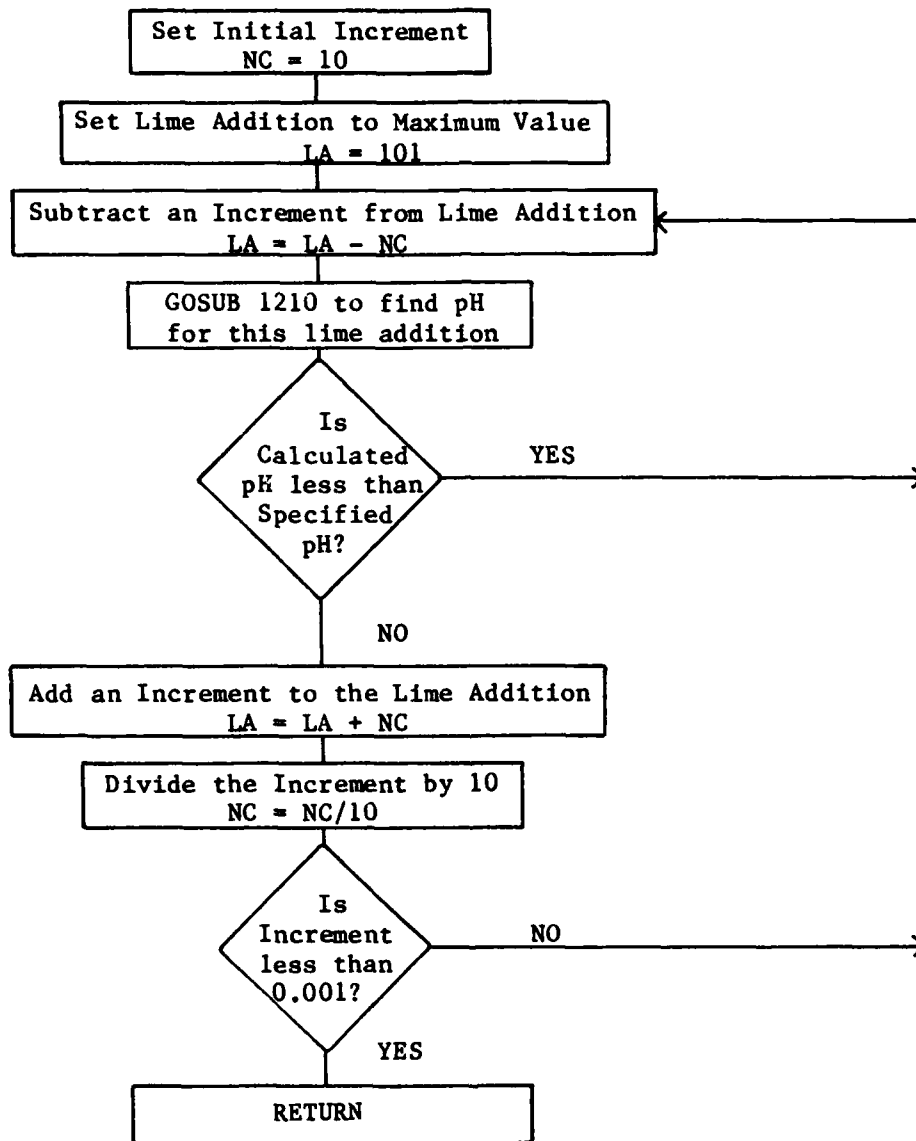


Figure 13. Logic for subroutine 1480

Initial Statement 1660

Purpose: Calculate the CO (carbon dioxide added) dosage required to produce a desired initial pH with LA (lime added) dosage constant

Referenced from line numbers 912 990 1030 1060

<u>Reference</u>	<u>Name</u>	<u>Definition</u>
1680	NC	Increment of CO (carbon dioxide added); initial value = 10.0
1680	CO	Carbon dioxide added to produce the desired initial pH; initial value = 0.0 mg/l
1700	PH	Initial pH produced by LA and CO
1700	VA	Desired initial pH
Return	1690 1710	

The logic for this subroutine is shown in Figure 14.

Initial Statement 1740

Purpose: Setting the maximum value of CO for a constant LA as input to pH calculations

Referenced from line number 860

<u>Reference</u>	<u>Name</u>	<u>Definition</u>
1760	CO	Maximum CO (carbon dioxide added); initial value = 101.0 mg/l as CaCO_3
Return	1770	

The logic for this subroutine is shown in Figure 15.

Initial Statement 1780

Purpose: Calculate the hydrogen concentration to produce an initial acidity, AD

Referenced from line number 1320

<u>Reference</u>	<u>Name</u>	<u>Definition</u>
1780	HI	Increment of hydrogen concentration; initial value = 0.01
1780	H	Hydrogen concentration

(Continued)

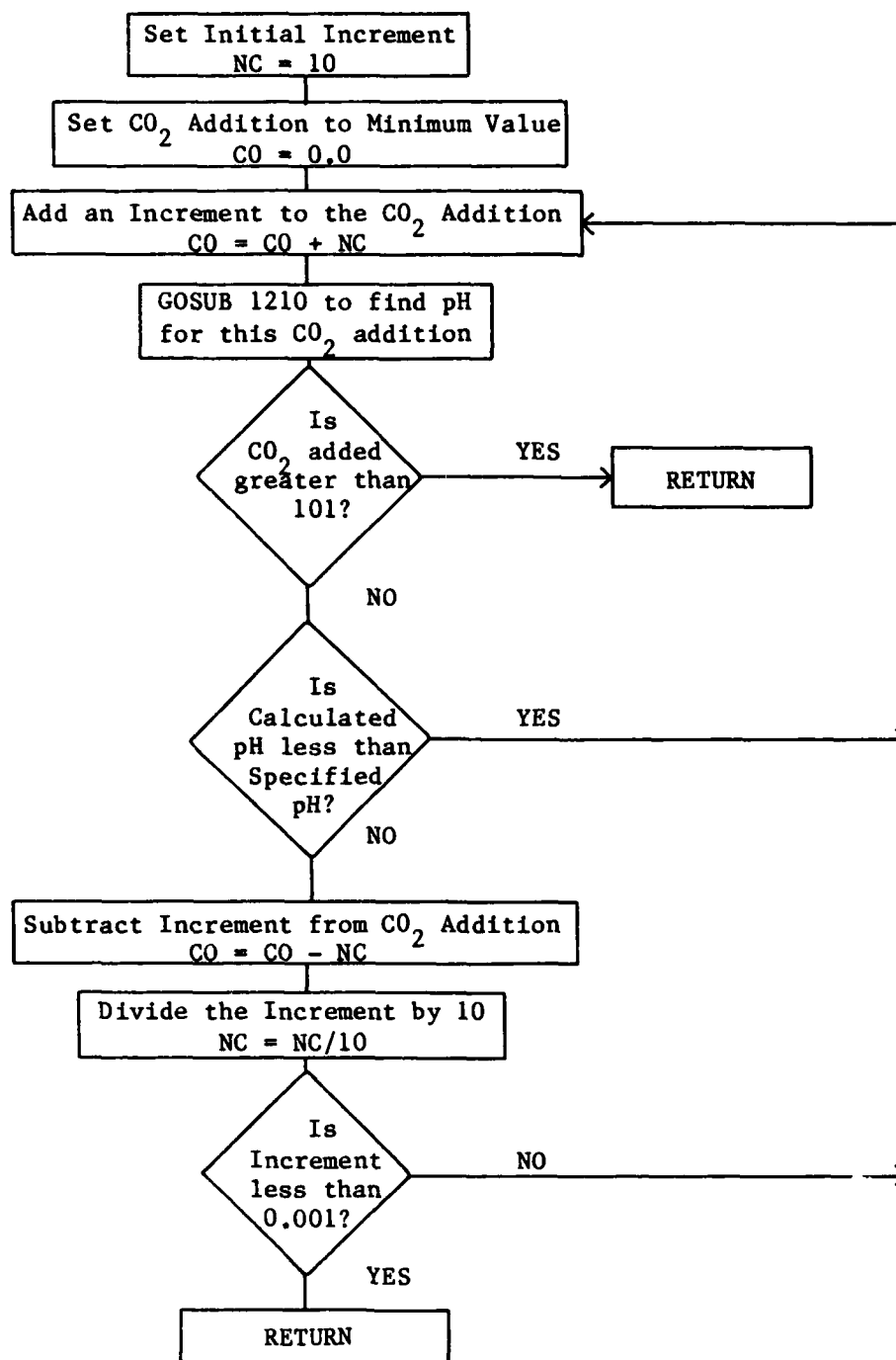


Figure 14. Logic for subroutine 1660

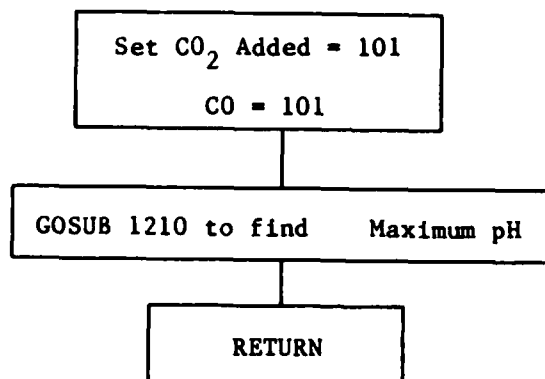


Figure 15. Logic for Subroutine 1740

<u>Reference</u>	<u>Name</u>	<u>Definition</u>
1790	ZC	Acidity produced by H
1810	AD	Initial acidity, mg/l as CaCO ₃
Return	1800	

The logic for this subroutine is shown in Figure 16.

Initial Statement 1880

Purpose: Calculate the hydrogen concentration to produce a final acidity of CI (AC)

Referenced from line number 1360

<u>Reference</u>	<u>Name</u>	<u>Definition</u>
1880	HI	Increment of hydrogen concentration; initial value = 0.01
1880	H	Hydrogen concentration
1890	ZC	Acidity produced by H
1900	CI	Final acidity, mg/l as CaCO ₃
Return	1900	

The subroutine logic is the same as that for subroutine 1780.

Initial Statement 29930

Purpose: Free form input routine

Referenced from line numbers 400 410 420 430 440 900
 2040 2050 2060

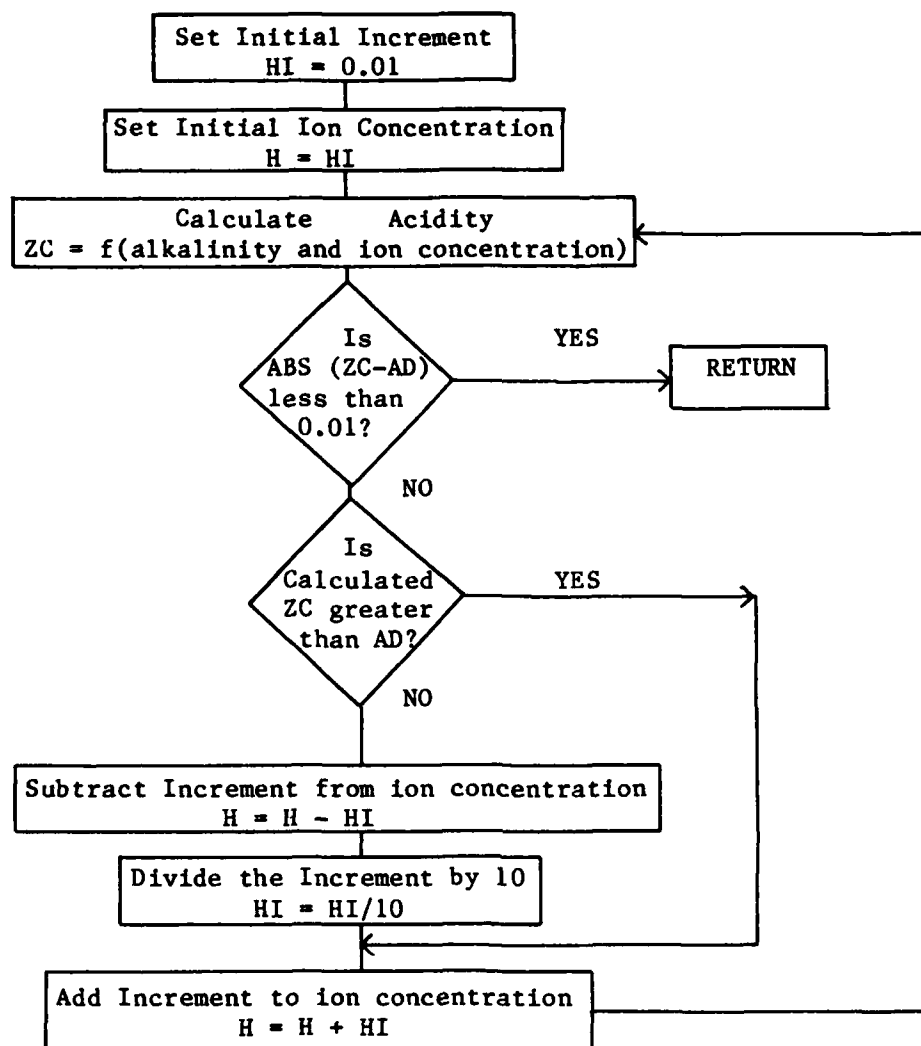


Figure 16. Logic for subroutine 1780

Reference	Name	Definition
30000	A\$	Input string
30000	V(20)	Return array for numeric values in input string A\$
30000	B\$(20)	Return array for alphanumeric words in input string A\$
30010	NN	Number of numeric values in input string A\$
30010	NW	Number of alphanumeric words in input string A\$
30010	NZ	Indicator for an alphanumeric word being currently processed (0 = No or 1 = Yes)

(Continued)

<u>Reference</u>	<u>Name</u>	<u>Definition</u>
30030	IZ\$	String containing two successive characters of input string A\$
30030	LZ\$	Left character of IZ\$
30030	RZ\$	Right character of IZ\$
30110	VZ\$	String containing the current number or word as it is being constructed one character at a time
30000	IZ	For next loop indicator
Return	30190	

Initial Statement 30230

Purpose: Output the lime added, carbon dioxide added, and interim pH

Referenced from line numbers 913 960 990 1010 1060

<u>Reference</u>	<u>Name</u>	<u>Definition</u>
30230	C\$	Output format string for lime added
30240	D\$	Output format string for carbon dioxide added
30250	SS(4)	Save array for LA (lime added) and CO (carbon dioxide) added
30250	KN	Indicator to proper subscript of the save array
Return	30280	

Input and Output

119. The input to the program consists of a description of the initial water quality, flow rate, desired precipitate, and purity of chemical feed.

The initial water quality is described by:

- a. Temperature.
- b. Total dissolved solids.
- c. Alkalinity.
- d. Calcium.
- e. pH.

The alkalinity and calcium concentration as well as the desired precipitate are entered as milligrams per litre as CaCO_3 . The user specifies effluent quality by entering the amount of precipitate as CaCO_3 .

120. For very high or low initial pH values, extremely high lime or

carbon dioxide dosage may be required. To assist the user in identifying if such a situation exists, the program prints the range of initial pH values for which chemical dosage will be less than 100 mg/l. Such high dosages will invalidate some of the assumptions made in developing the solution procedure.

121. In practice lime and carbon dioxide are not fed as 100 percent pure chemical. To calculate the feed rate of the chemical as commercially available, the user must enter the purity in percent. Since hydrated (slaked) lime and quicklime are usually of different purity, the user should enter the purity of lime to be fed at the treatment plant of interest. To determine the actual feed rate in pounds per hour, the program user must enter the actual flow rate in million gallons per day.

122. The output from the program consists of the lime and carbon dioxide dose in milligrams per litre as CaCO_3 . If the dose of one of the chemicals is zero, then the heading is not printed. If the user enters a positive value for chemical purity, the program calculates the dosage as milligrams per litre as commercially available chemical. The program also prints the interim and final pH, and the final calcium hardness and alkalinity as milligrams as CaCO_3 . The user can also enter the flow rate so that the program can calculate the dosage in pounds per hour of the commercial chemical to be fed.

Users Guide for IBM Version

Execution

123. The Water Conditioning Program is executed directly from PC-DOS. Ensure that DOS is operational on the IBM personal computer. Instructions for "booting" the operating system are contained in the publication "IBM Personal Computer Guide to Operations" supplied with the computer. This booting can be accomplished by placing a DOS diskette (label side up--read/write slot in first) in drive A which is normally on the left side. With the DOS diskette in place, either turn on the power or depress the <Ctrl><Alt> keys simultaneously. As instructed by the display, enter the date and the time or respond with two <ENTER>'s. The display of the prompt A> indicates that DOS is operational.

124. Place the Water Conditioning diskette in disk drive B (normally on the right side). To list the program on the printer, first toggle the printer

on by depressing the <Ctrl><PrtSc> keys simultaneously then type

TYPE B:CAC03.BAS

125. The printer may be toggled off by once again depressing the <Ctrl><PrtSc> keys simultaneously. To run the program respond to the A> prompt by typing

B:CAC03

Data entry and program output

126. Upon execution the program will present a title screen which will inform the user that the Water Conditioning Program is indeed being executed. Depressing the <Space Bar> will release this screen and allow the execution to continue. Next a data screen will be displayed indicating the data items required to describe the initial condition of the water. The form of this screen is shown below:

WATER CONDITIONING PROGRAM

TEMPERATURE? DEGREES C
TOTAL DISSOLVED SOLIDS? MG/L AS CAC03
DESIRED PRECIPITATE? MG/L AS CAC03
ALKALINITY? MG/L AS CAC03
CALCIUM? MG/L AS CAC03
INITIAL PH?

127. Each data area will be highlighted in turn with the cursor placed in that position. The user should enter the data for the highlighted area along with an <ENTER>. After entry of the initial calcium content, the program will calculate and display the reasonable pH limits. These limits are based on the addition of 101 mg/l CaCO_3 or of CO_2 . While the program may produce results for pH values outside this range, the large chemical requirements may violate the assumptions on which the program algorithms are based. Following the entry of the initial pH, the solution of the problem will be displayed on the bottom half of the screen. For a typical problem the display would appear as shown below:

WATER CONDITIONING PROGRAM

TEMPERATURE?	25 DEGREES C	
TOTAL DISSOLVED SOLIDS?	40 MG/L AS CAC03	
DESIRED PRECIPITATE?	4 MG/L AS CAC03	FINAL VALUES
ALKALINITY?	40 MG/L AS CAC03	46.0
CALCIUM?	30 MG/L AS CAC03	36.0
INITIAL PH?	8.0 (PRACTICAL PH RANGL 5.92 TO 11.10)	8.6

ADD 10.0 MG/L OF LIME AS CAC03 : 7.4 MG/L AS CA(OH)2 : 5.6 MG/L AS CAO
ADD 13.1 MG/L OF C02 AS CAC03 : 5.8 MG/L AS C02
INTERIM PH WILL BE 9.0

^PrtSc - HARD COPY: 'C' - FEED RATES: Space Bar - NEXT PROBLEM: 'Q' - QUIT

As shown above, the bottom line of the display indicates the options available at this point. These options are as follows:

<Shift><PrtSc> - Produce a hard copy of the screen on the printer.
<Space Bar> - Present a new data screen, thus allowing the user to continue with a new problem.
<Q> - Terminate the execution of the program.
<C> - Calculate feed rates in terms of commercially available chemicals.

The data screen and resulting output for the <C> option are shown below:

WATER CONDITIONING PROGRAM

PURITY: LIME? 90% C02? 87%
FLOW RATE 25.0 MGD

AS COMMERCIALY AVAILABLE:

ADD 8.2 MG/L OF LIME AS CA(OH)2: 6.2 MG/L AS CAO
ADD 6.6 MG/L OF C02 AS C02

AS COMMERCIALY AVAILABLE:

ADD 71.4 LB/HR OF LIME AS CA(OH)_2 : 54.1 LB/HR AS CAO

ADD 57.7 LB/HR OF CO_2 AS CO_2

APrt Sc - HARD COPY: Space Bar - NEXT PROBLEM: 'Q' - QUIT

An <ENTER> response to any data request will produce a zero entry for that item. Thus, <ENTER> should only be used for an unnecessary chemical purity request or for the flow rate if pounds per hour calculations are not desired.

Users Guide for Apple Version

128. The Water Conditioning Program is written in Applesoft BASIC so the user must be sure that the interpreter or compiler for this language is available before running the program. For most Apple computers, the system is automatically in Applesoft BASIC when it is booted (i.e. when the power is turned on or the machine is reset) and the System Master disc is in the disc drive. The user will receive a] prompt at this time. The user should then place the program disc in the disc drive.

129. To begin the program, the user enters RUN CAC03 and the program responds with DO YOU WANT HARD COPY(Y/N)?. If the user responds N, the prompts and output are displayed only on the screen. If the user types Y, prompts and output are displayed on the screen and the printer simultaneously. If the users enters Y, the printer must be turned on and must be in the ON LINE mode if the user has the option of local or on-line printing.

130. The program then prints a title screen and instructs the user to type RETURN TO CONTINUE. When the user types return, the program title is printed and the user is queried for

TEMPERATURE(DEG C)?

TOTAL DISSOLVED SOLIDS (MG/L)?

DESIRED PRECIPITATE (MG/L AS CACO_3)?

ALKALINITY (MG/L AS CACO_3)?

CALCIUM (MG/L AS CACO_3)?

131. The values for alkalinity and calcium refer to the initial concentrations as opposed to the final concentrations which are determined by the program. Once the user enters the calcium concentration, the program begins to flash the word STANDBY as it performs some calculations to determine the range of initial pH values which will result in reasonable chemical doses. This step takes several minutes in interpretive BASIC.

132. Eventually, the program will print the ALLOWABLE PH RANGE. These values are only a guide for initial pH values that will yield reasonable chemical dosages. The user is then prompted for INITIAL PH?. Upon entering this value, the user will once again receive the STANDBY message as the program computes chemical doses.

133. After several minutes, the program will print CHEMICAL DOSAGE BASED ON PURE CHEMICAL and will print the chemical doses of lime and carbon dioxide in milligrams per litre as CaCO_3 based on the chemicals being 100 percent pure. The program will also print the final calcium and alkalinity as CaCO_3 and the interim and final pH. In cases in which the desired precipitate can be obtained by adding only lime, but the interim pH will be in the 8.2 to 8.5 range, the program calculates another solution with both lime and carbon dioxide feed which avoids this interim pH range.

134. Since the user does not purchase or feed chemical of 100 percent purity, and feed equipment feeds chemical as actual chemical not as CaCO_3 , the user must determine actual feed rates in pounds per hour. The program instructs the user TYPE Q TO QUIT - C FOR CHEM FEED - RETURN FOR NEW PROBLEM?. If the user enters Q, the program stops. If the user enters any other character other than Q or C, the program returns to the start and requests data for a new problem. If the user enters C, the program instructs the user to enter data on chemical purity of the feed chemicals and the actual flow rate (not design flow rate for the plant). The program prints

PURITY LIME(%)?

PURITY CO2(%)?

FLOW RATE (MGD)?

135. The program then calculates the dosage in terms of lime and carbon dioxide as commercially available and prints this output in milligrams per litre. If a nonzero value is entered for flow rate, the program also

calculates the feed rate in pounds per hour as commercially available chemical. The user is then given the option of stopping the program or running another problem. The program instructs the user, TYPE Q TO QUIT - RETURN FOR A NEW PROBLEM.

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APPENDIX A: WATER STABILIZATION DIAGRAMS

1. The water stabilization diagrams presented in this appendix may be used to determine the doses of lime and carbon dioxide required to stabilize virtually all waters of interest to the potable water supply industry. The diagrams were designed and constructed to ensure that the following interim water quality criteria are always met:

Alkalinity	≥ 40 mg/l as CaCO_3
Calcium hardness	≥ 40 mg/l as CaCO_3
pH	≤ 9.2
Precipitation potential	4 mg/l as CaCO_3

In addition, the diagrams provide a warning whenever the interim pH falls within the 8.0 to 8.5 range since the portion of the "lime required" curves corresponding to this pH range are shown in dotted rather than solid lines.

2. To use the diagrams the user need only know the temperature ($^{\circ}\text{C}$), total dissolved solids concentration (mg/l), pH, alkalinity (mg/l as CaCO_3), and calcium hardness (mg/l as CaCO_3) of the water to be stabilized. This information may be obtained through routine analyses performed at virtually all potable water treatment plants. Then, using Table A1, the correct diagram can be selected.

3. In the typical case the user should select the proper diagram (or diagrams if interpolation is necessary) based upon the total dissolved solids, water temperature, and alkalinity of interest. Then, knowing the initial pH (i.e. the pH of the untreated water), it is possible to read the lime and carbon dioxide doses required directly from the diagram. The dotted/solid lines on the left side of the diagrams are the "lime required" curves. The dashed lines on the right side of the diagrams are the "carbon dioxide required" curves. The left ordinate is labeled with respect to lime, while the right ordinate is labeled with respect to carbon dioxide. However, since the same units of expression (mg/l as CaCO_3) and scale (1 inch = 10 mg/l) are used on both ordinates, the dose of either chemical may be read from either ordinate. It is important to realize that the chemical doses shown are expressed in terms of calcium carbonate. Thus, it is necessary to make the appropriate conversions to other units of expression (e.g. lime as commercially available

product) depending upon the specific chemical form (e.g. hydrated or quick-lime) to be used in practice.

4. The diagrams are arranged in ascending numerical order, first according to total dissolved solids concentration, then according to temperature, and finally according to alkalinity. In some cases, more than one diagram is provided for a given combination of total dissolved solids, temperature, and alkalinity. In these instances the diagrams are arranged in ascending numerical order with respect to calcium hardness.

5. The relative magnitude of the effect of total dissolved solids concentration on the lime and carbon dioxide doses required for stabilization is such that it is not necessary to interpolate for intermediate values. Rather, the user should select a diagram for the total dissolved solids concentration closest to the actual value and use it directly.

6. Temperature has a somewhat greater effect, and, if the actual temperature varies by more than a few degrees from the most appropriate diagram, linear interpolation between diagrams may be used.

7. Linear interpolation may also be used for values of calcium hardness falling between the curves plotted on the diagrams, and for values of alkalinity between those shown on the diagrams. The specific values of alkalinity and calcium hardness used to construct the diagrams were selected to facilitate interpolation for intermediate values.

Table A1
Master Table for Selection of Water Stabilization Diagrams

Total Dissolved Solids mg/l	Temperature °C	Alkalinity mg/l as CaCO ₃	Calcium Hardness Range mg/l as CaCO ₃	Diagram
40	5	20	1-20	A1
		30	1-30	A2
		40	1-40	A3
		50	1-40	A4
		60	1-40	A5
		80	1-40	A6
		100	1-40	A7
	10	20	1-20	A8
		30	1-30	A9
	15	20	1-20	A10
		30	1-30	A11
		40	1-40	A12
		50	1-40	A13
		60	1-40	A14
		80	1-40	A15
		100	1-40	A16
	20	20	1-20	A17
		30	1-30	A18
	25	20	1-20	A19
		30	1-30	A20
		40	1-40	A21
		50	1-40	A22
		60	1-40	A23
		80	1-40	A24
		100	1-40	A25
400	5	40	1-40	A26
			40-200	A27
			200-300	A28
		60	1-80	A29
			80-300	A30
		80	1-50	A31
			50-300	A32
		100	1-40	A33
			40-300	A34
		120	1-40	A35
			40-300	A36
		140	1-40	A37
			40-300	A38
		160	1-40	A39
			40-300	A40

(Continued)

(Sheet 1 of 3)

Table A1 (Continued)

Total Dissolved Solids mg/l	Temperature °C	Alkalinity mg/l as CaCO ₃	Calcium Hardness Range mg/l as CaCO ₃	Diagram
400	5	180	1-40	A41
			40-300	A42
		200	1-40	A43
			40-300	A44
	15	40	1-80	A45
			80-300	A46
		60	1-40	A47
			40-300	A48
		80	1-40	A49
			40-300	A50
		100	1-40	A51
			40-300	A52
		120	1-40	A53
			40-300	A54
		140	1-40	A55
			40-300	A56
		160	1-40	A57
			40-300	A58
		180	1-40	A59
			40-300	A60
		200	1-40	A61
			40-300	A62
	25	40	1-40	A63
			40-300	A64
		60	1-40	A65
			40-300	A66
		80	1-40	A67
			40-300	A68
		100	1-40	A69
			40-300	A70
		120	1-40	A71
			40-300	A72
		140	1-40	A73
			40-300	A74
		160	1-40	A75
			40-300	A76
		180	1-40	A77
			40-300	A78
		200	1-40	A79
			40-300	A80

(Continued)

(Sheet 2 of 3)

Table A1 (Concluded)

Total Dissolved Solids mg/l	Temperature °C	Alkalinity mg/l as CaCO ₃	Calcium Hardness Range mg/l as CaCO ₃	Diagram
1200	5	100	40-500	A81
		120	40-500	A82
		140	40-500	A83
		160	40-500	A84
		180	40-500	A85
		200	40-500	A86
		240	40-500	A87
		280	40-500	A88
		320	40-500	A89
		360	40-500	A90
		400	40-500	A91
	15	100	40-500	A92
		120	40-500	A93
		140	40-500	A94
		160	40-500	A95
		180	40-500	A96
		200	40-500	A97
		240	40-500	A98
		280	40-500	A99
		320	40-500	A100
		360	40-500	A101
		400	40-500	A102
	25	100	40-500	A103
		120	40-500	A104
		140	40-500	A105
		160	40-500	A106
		180	40-500	A107
		200	40-500	A108
		240	40-500	A109
		280	40-500	A110
		320	40-500	A111
		360	40-500	A112
		340	40-500	A113

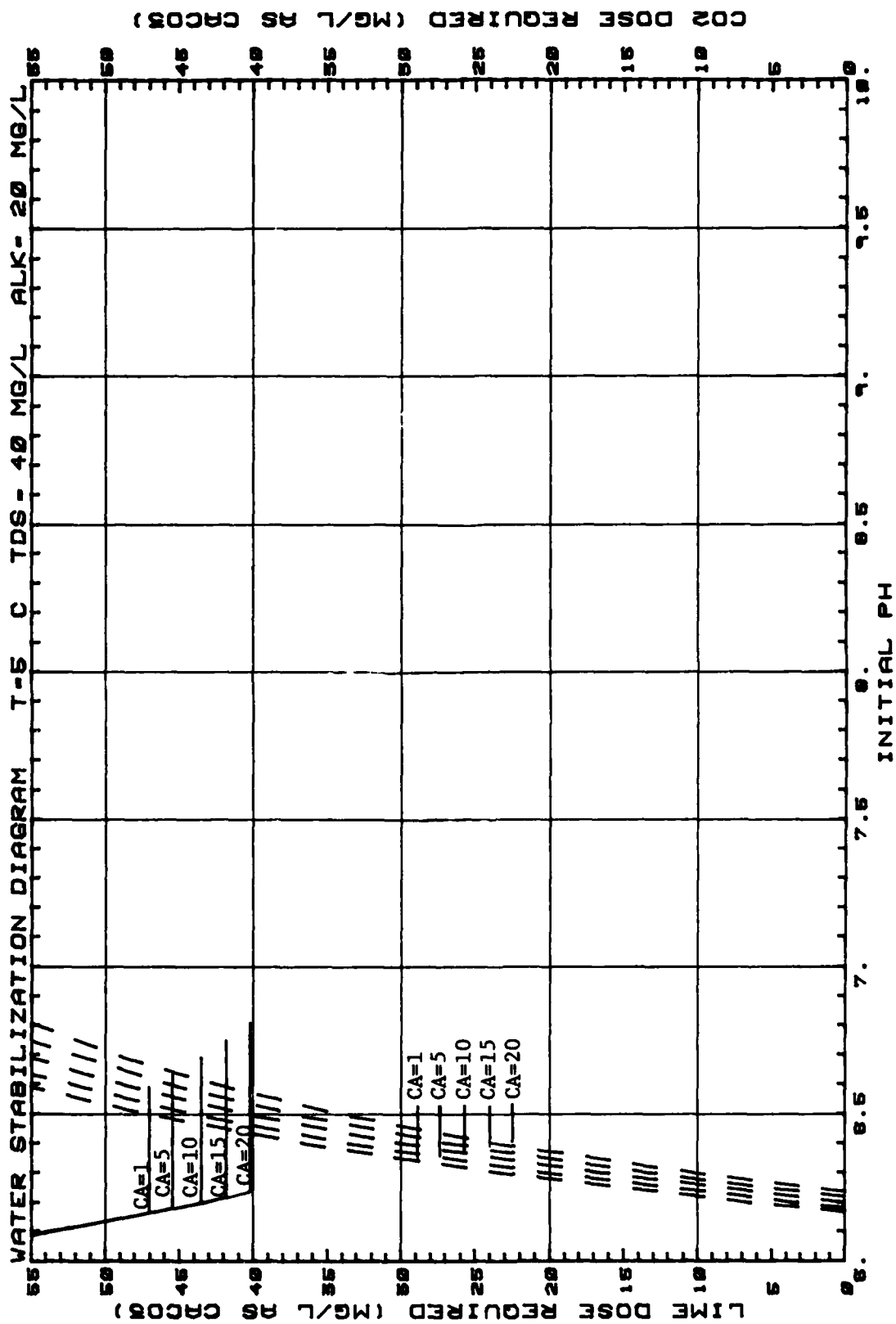


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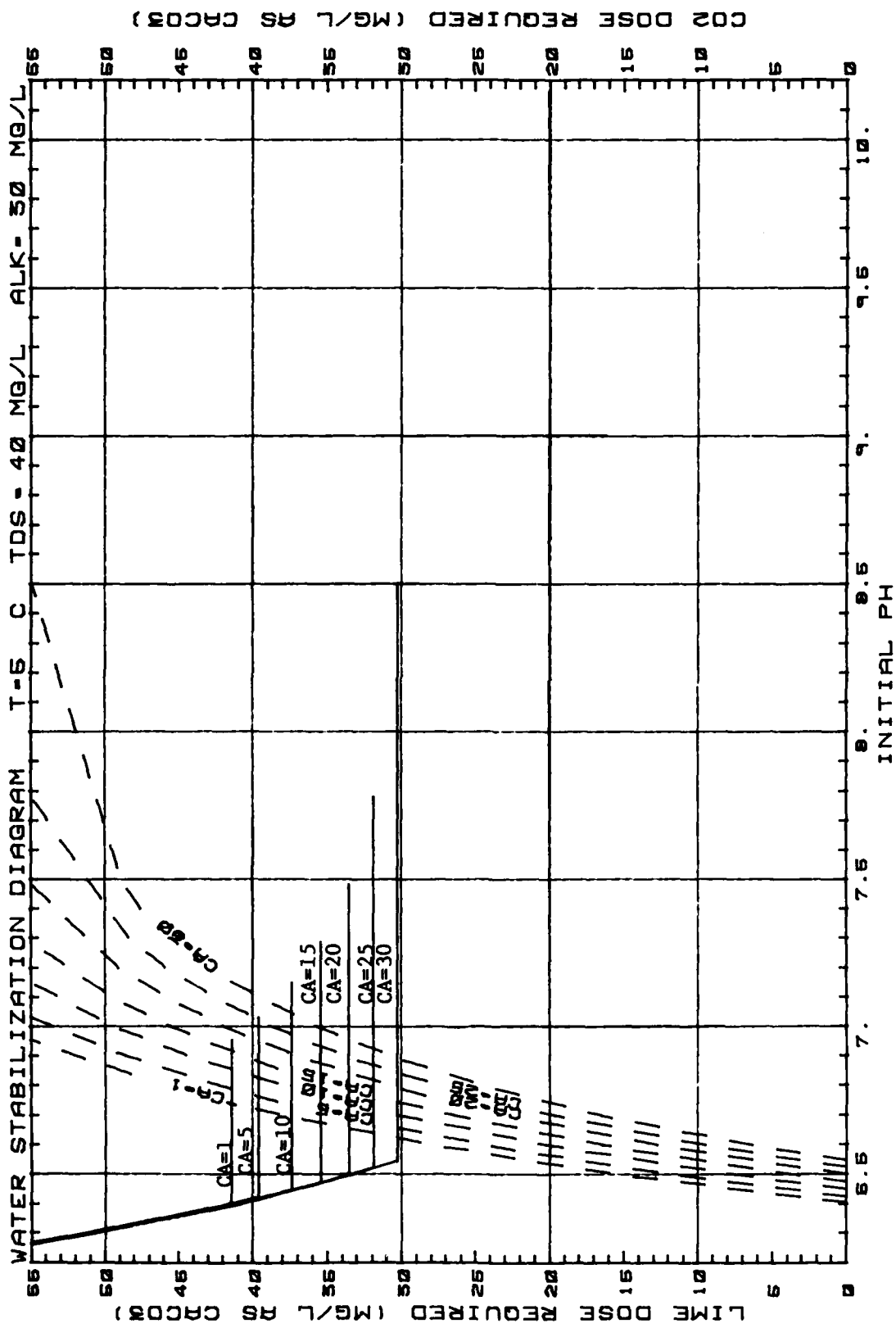


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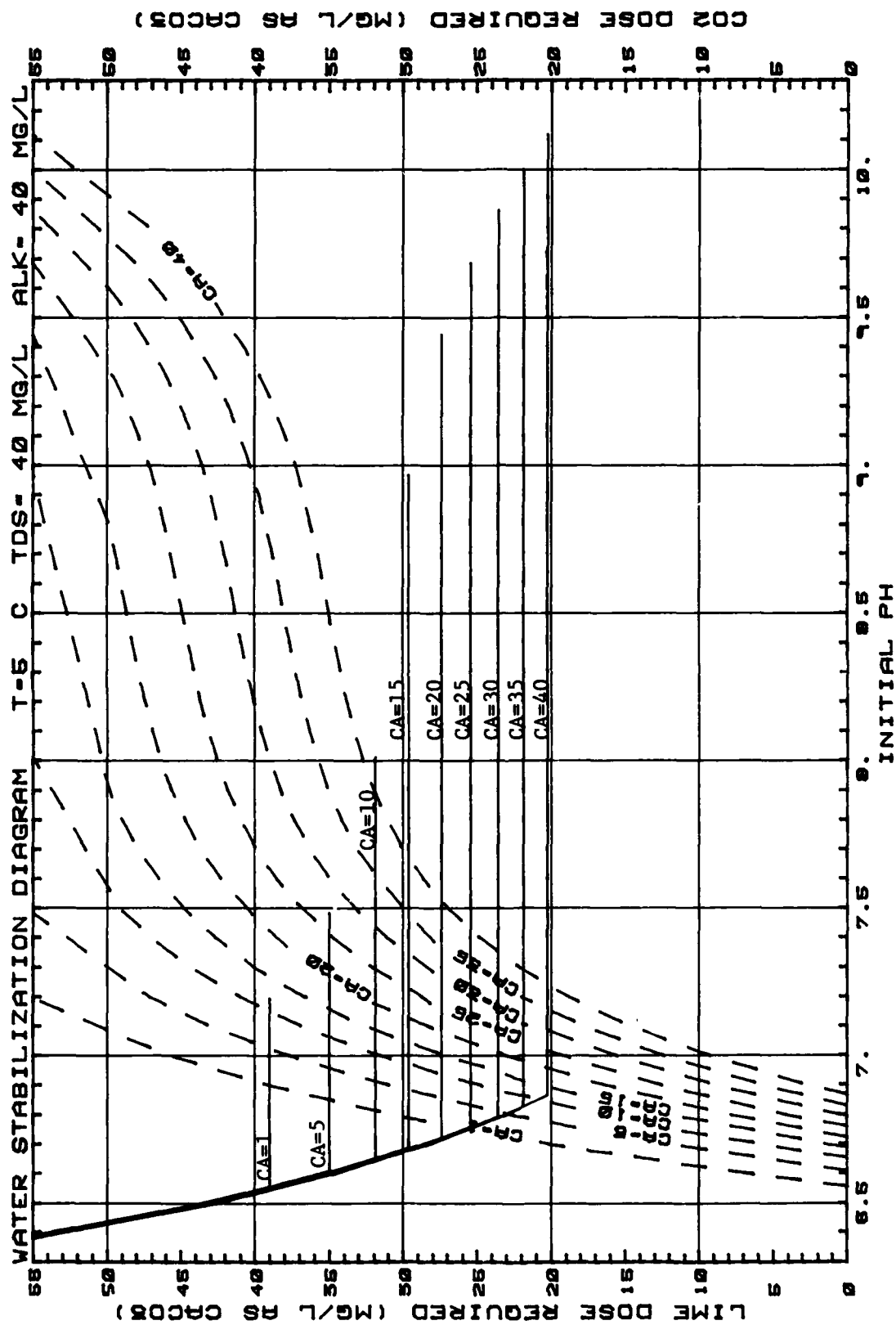


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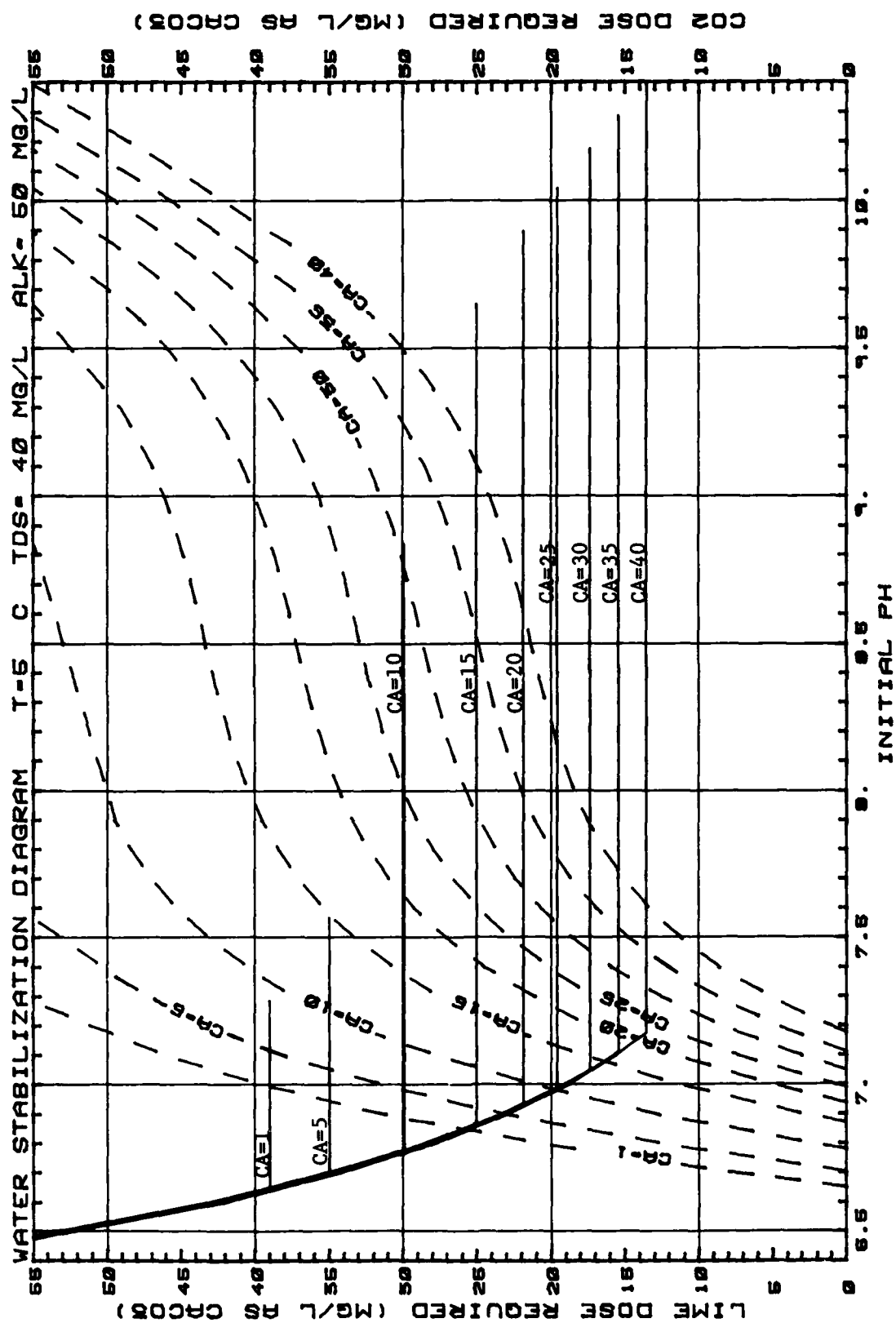


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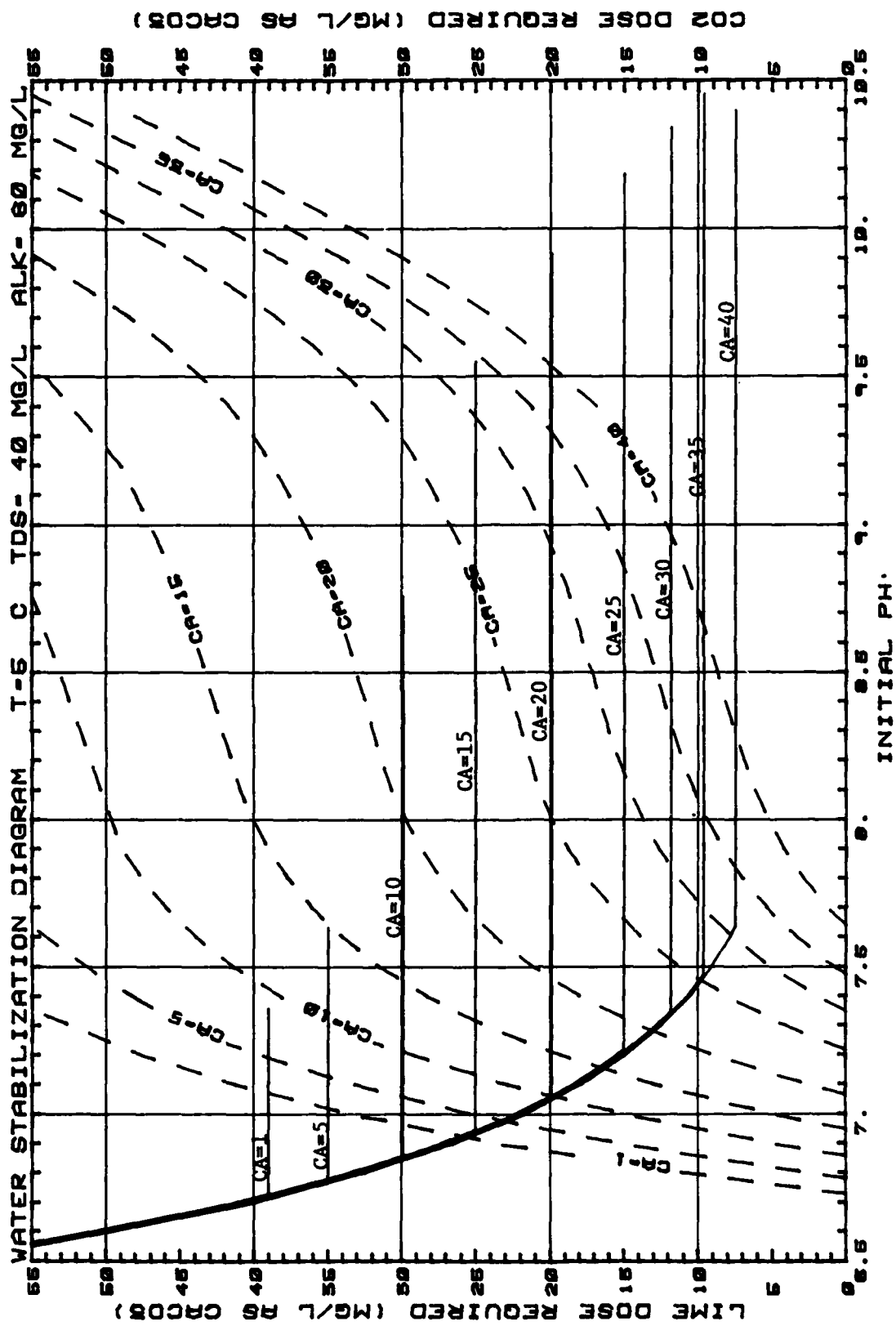


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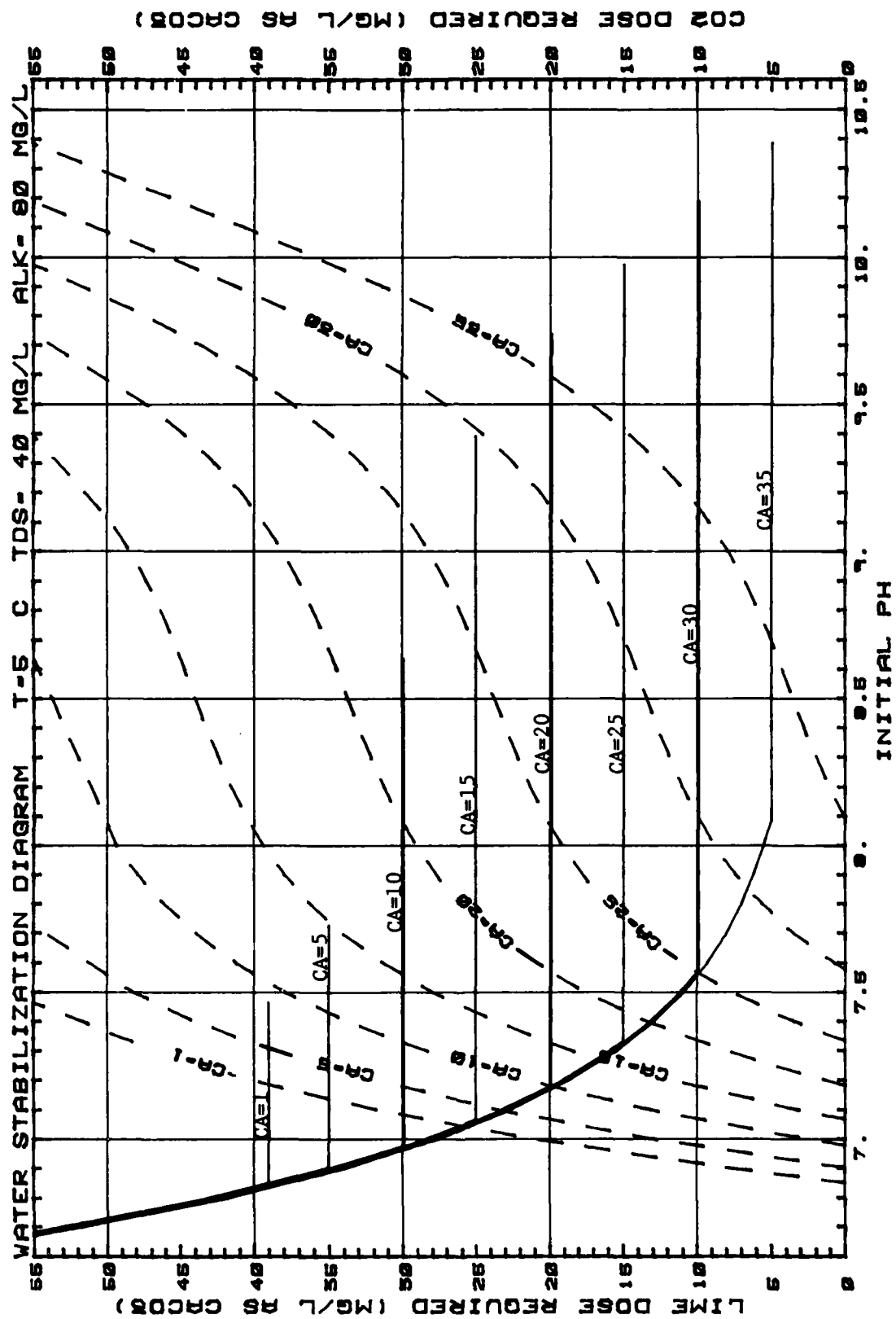


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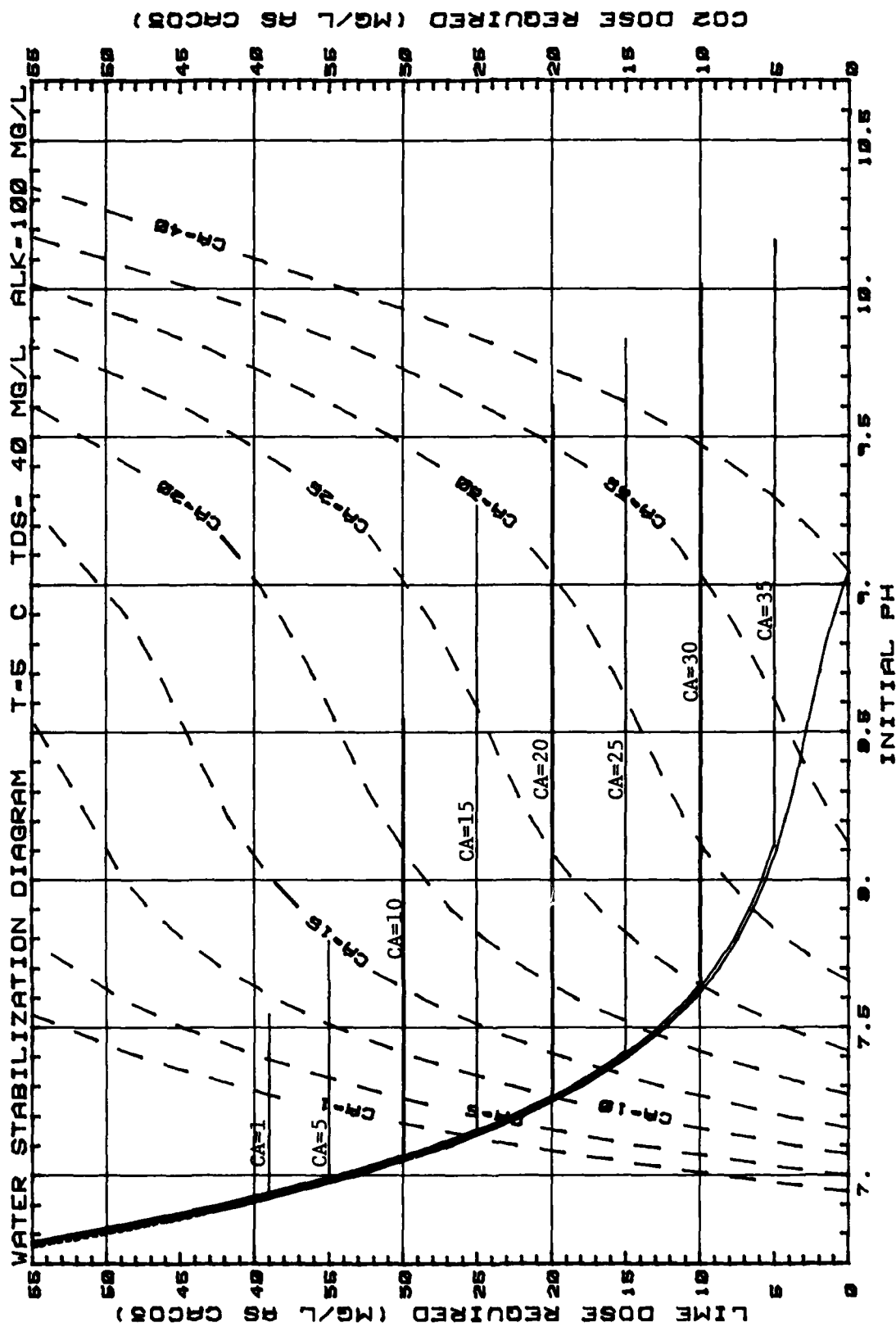


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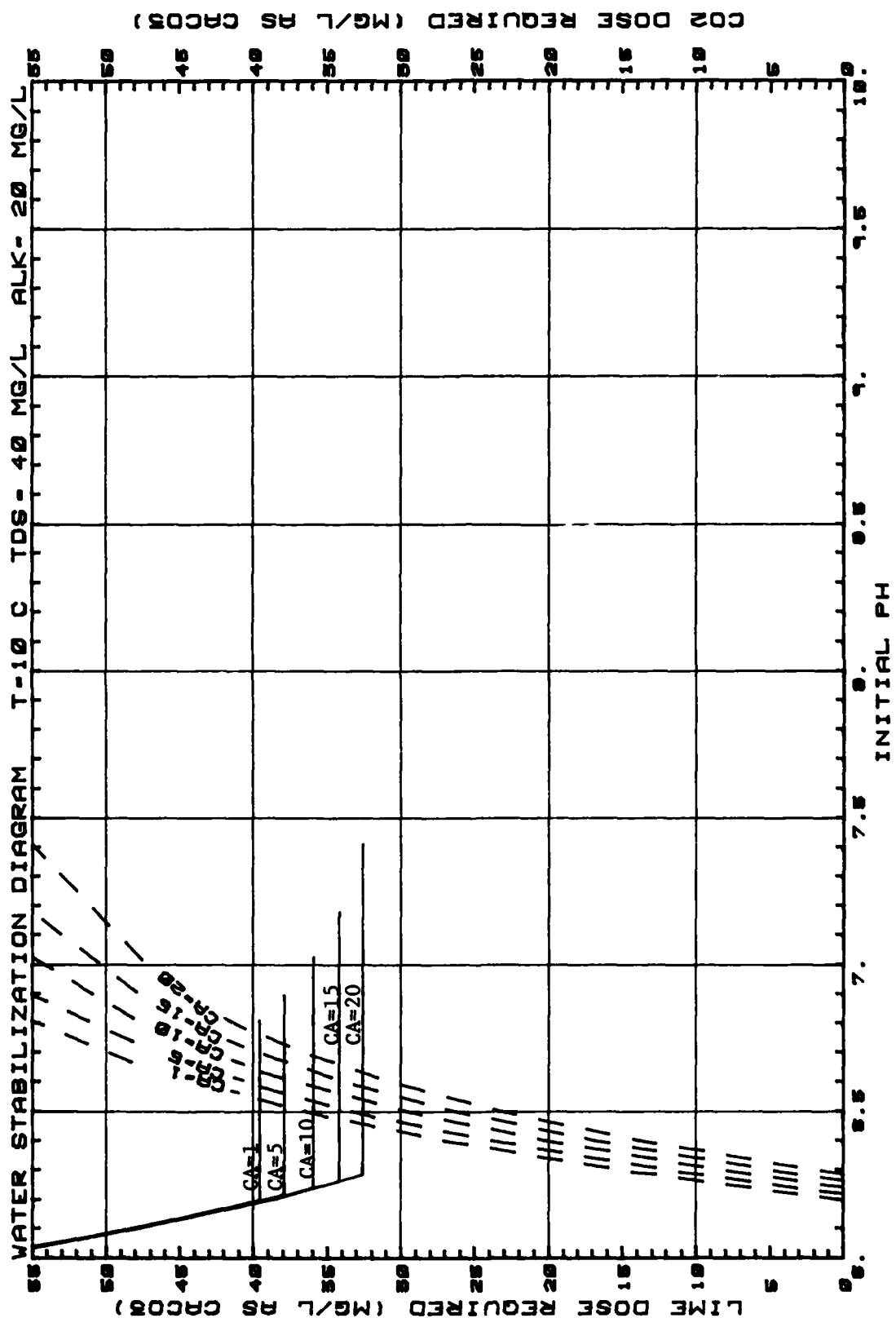


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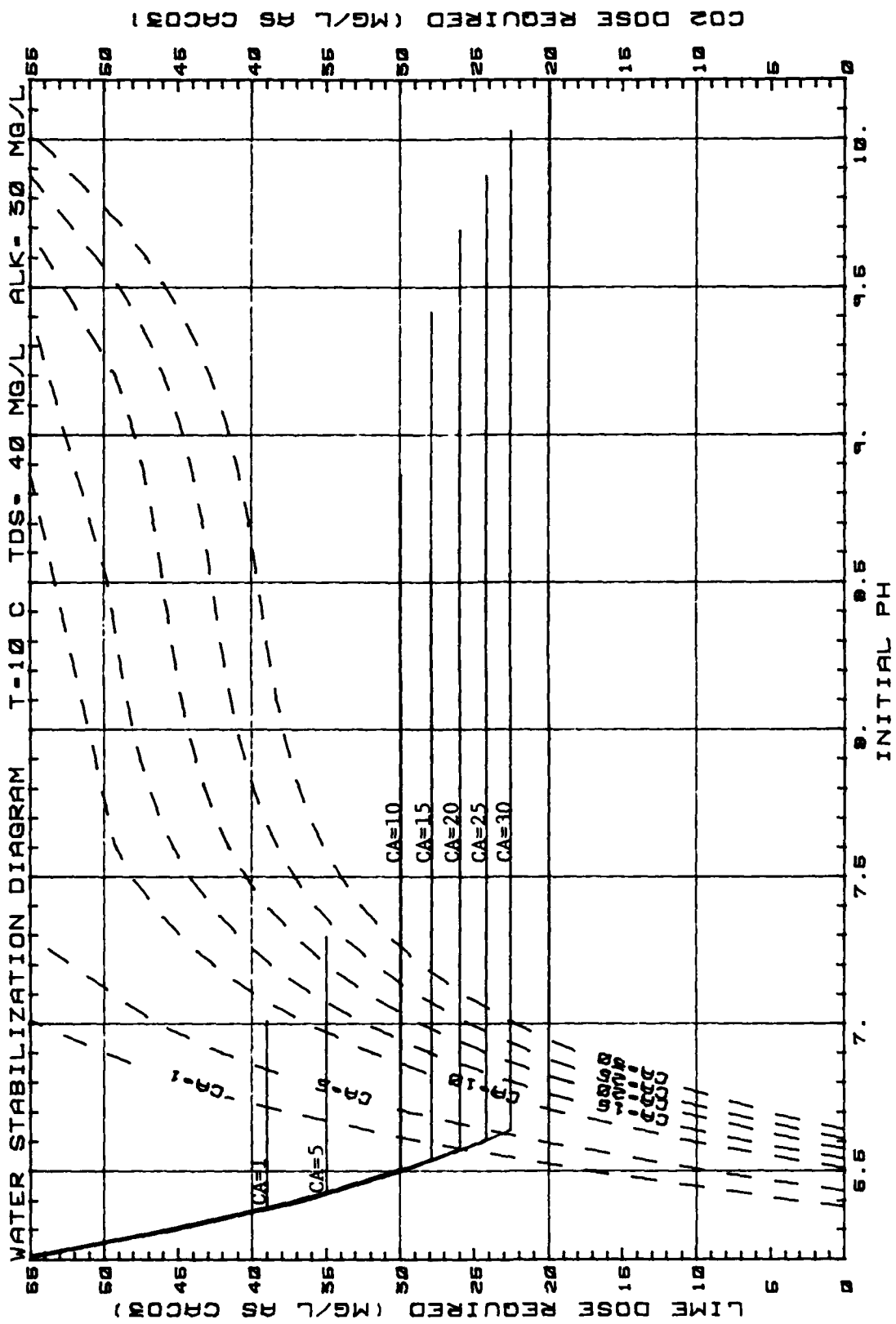


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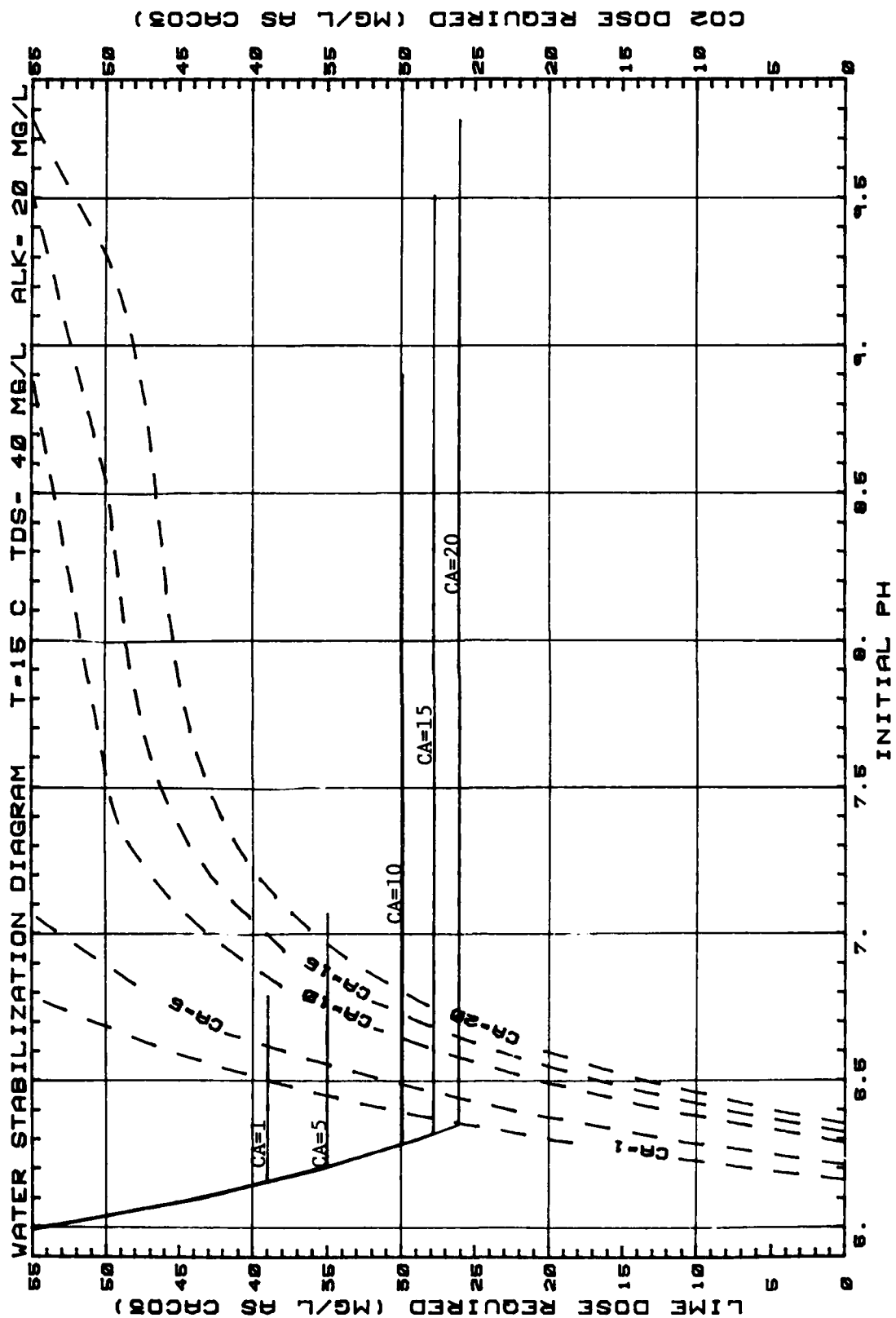
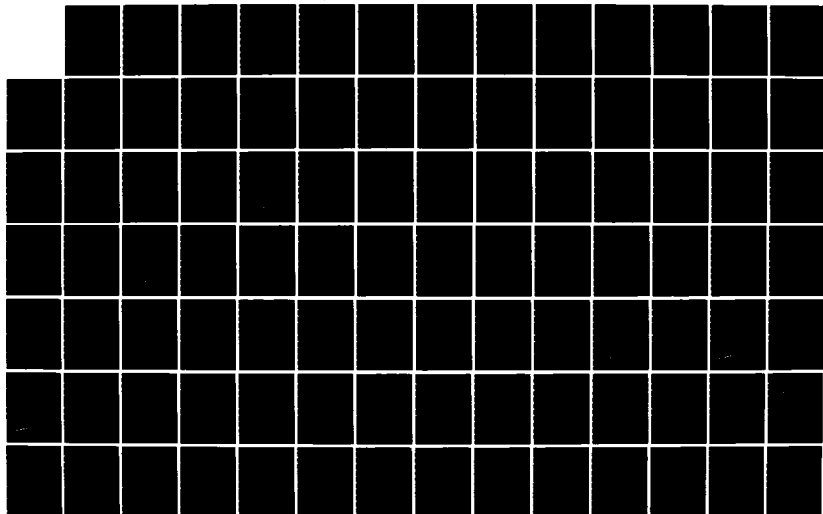
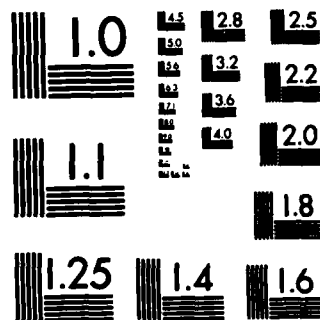


DIAGRAM A10

AD-A144 670 SIMPLIFIED PROCEDURE FOR CALCULATING CHEMICAL DOSES FOR 2/3
WATER STABILIZATI. (U) ARMY ENGINEER WATERWAYS
EXPERIMENT STATION VICKSBURG MS ENVIR.
UNCLASSIFIED J M MORGAN ET AL. JUN 84 WES/TR/EL-84-6 F/G 13/2 NL





MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

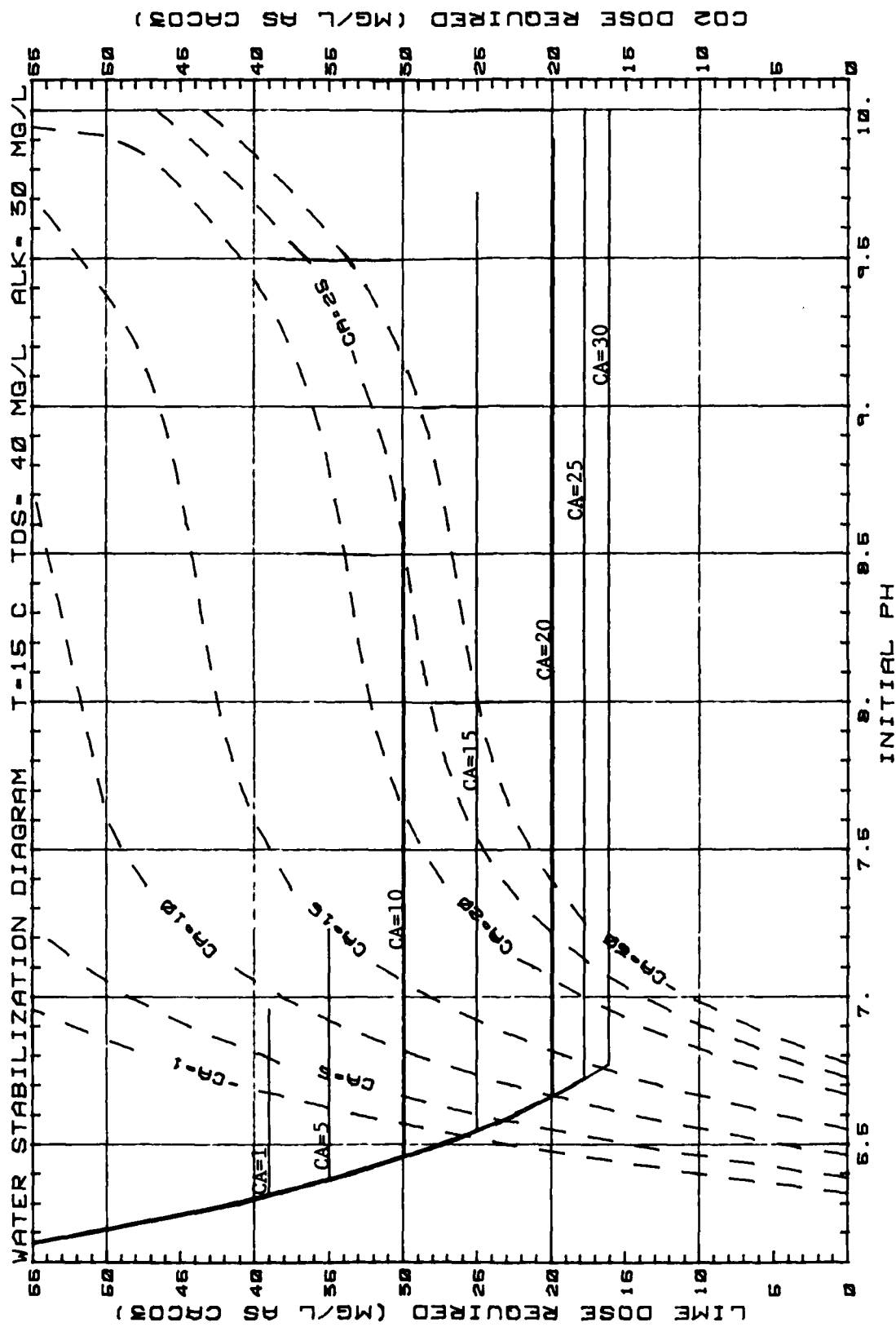


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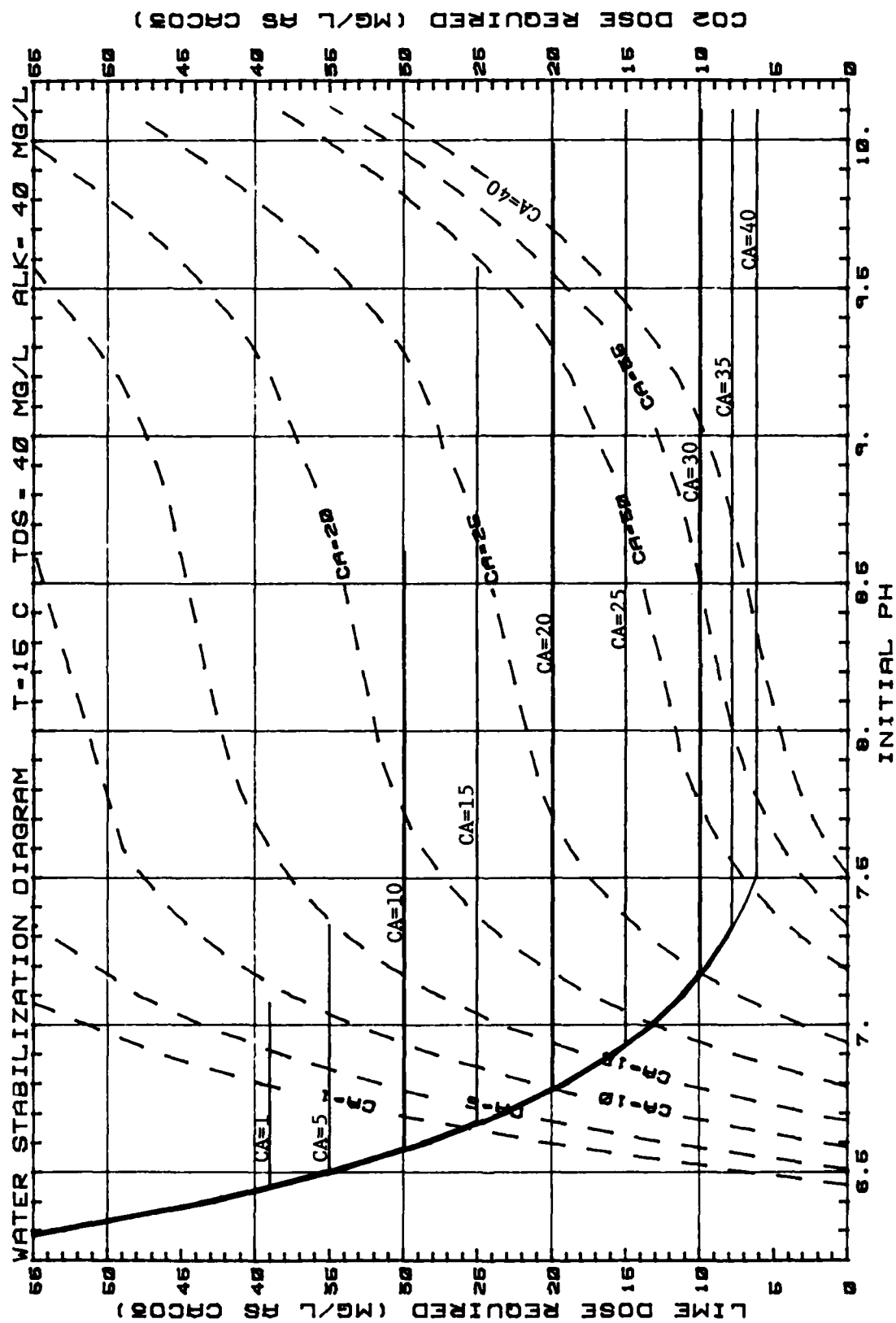


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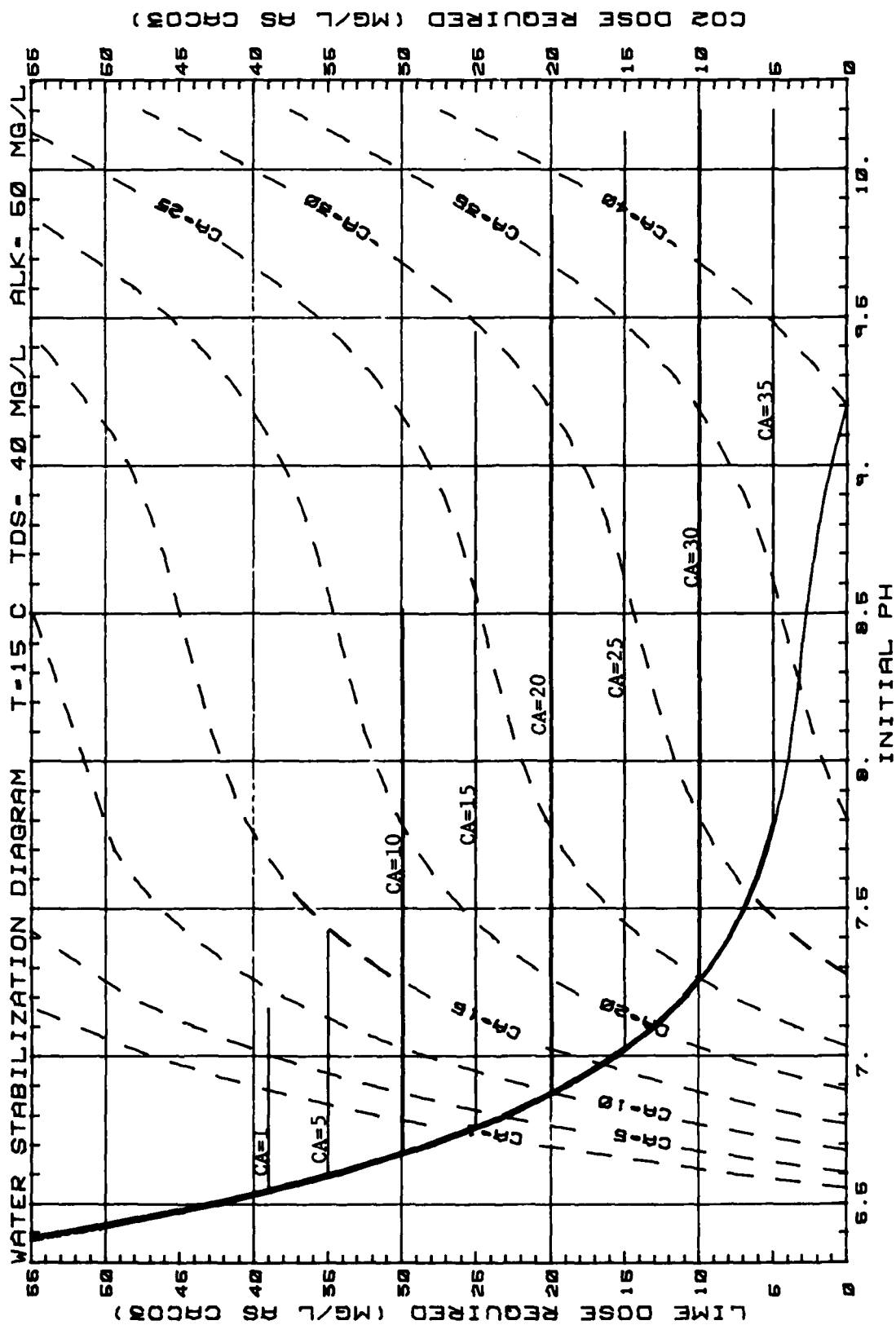


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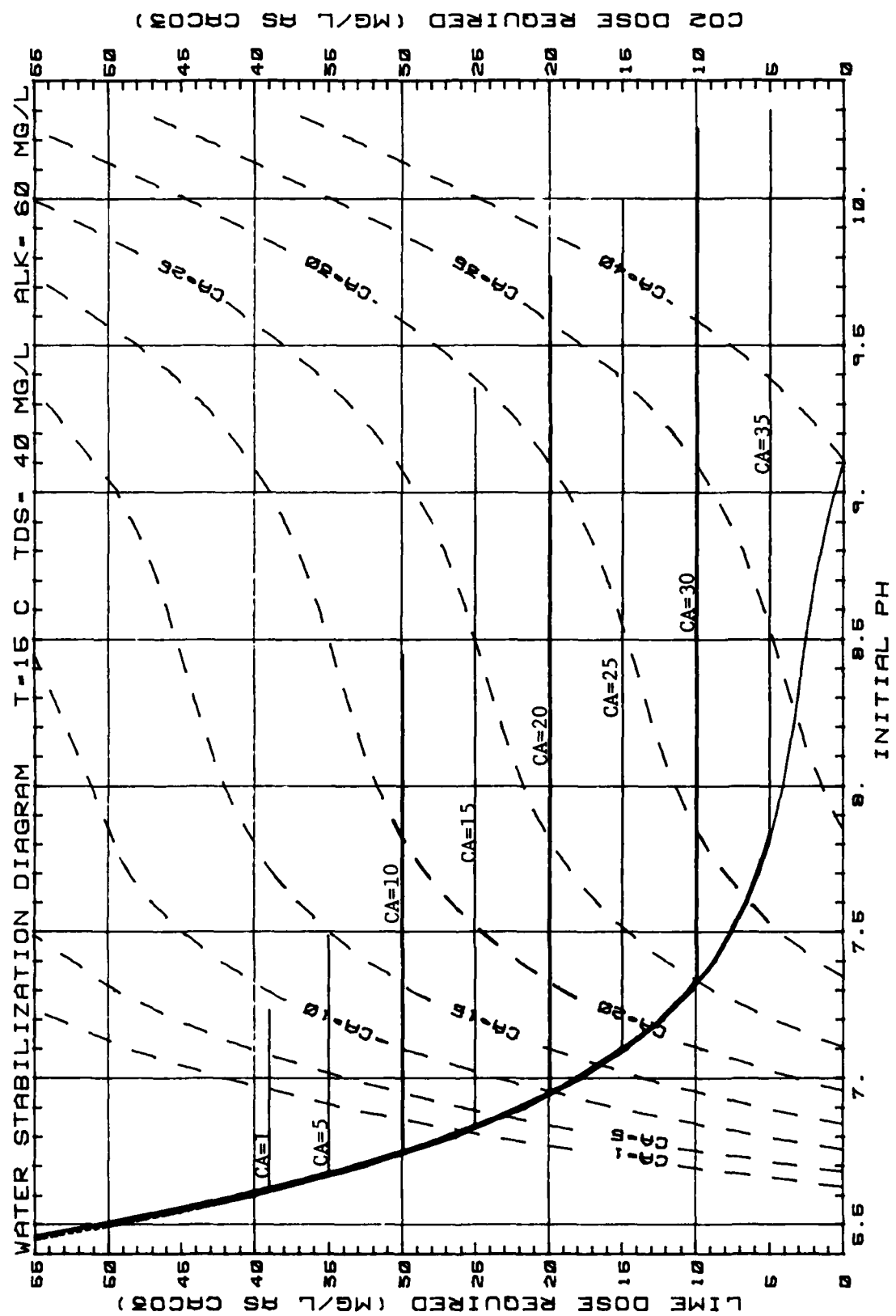


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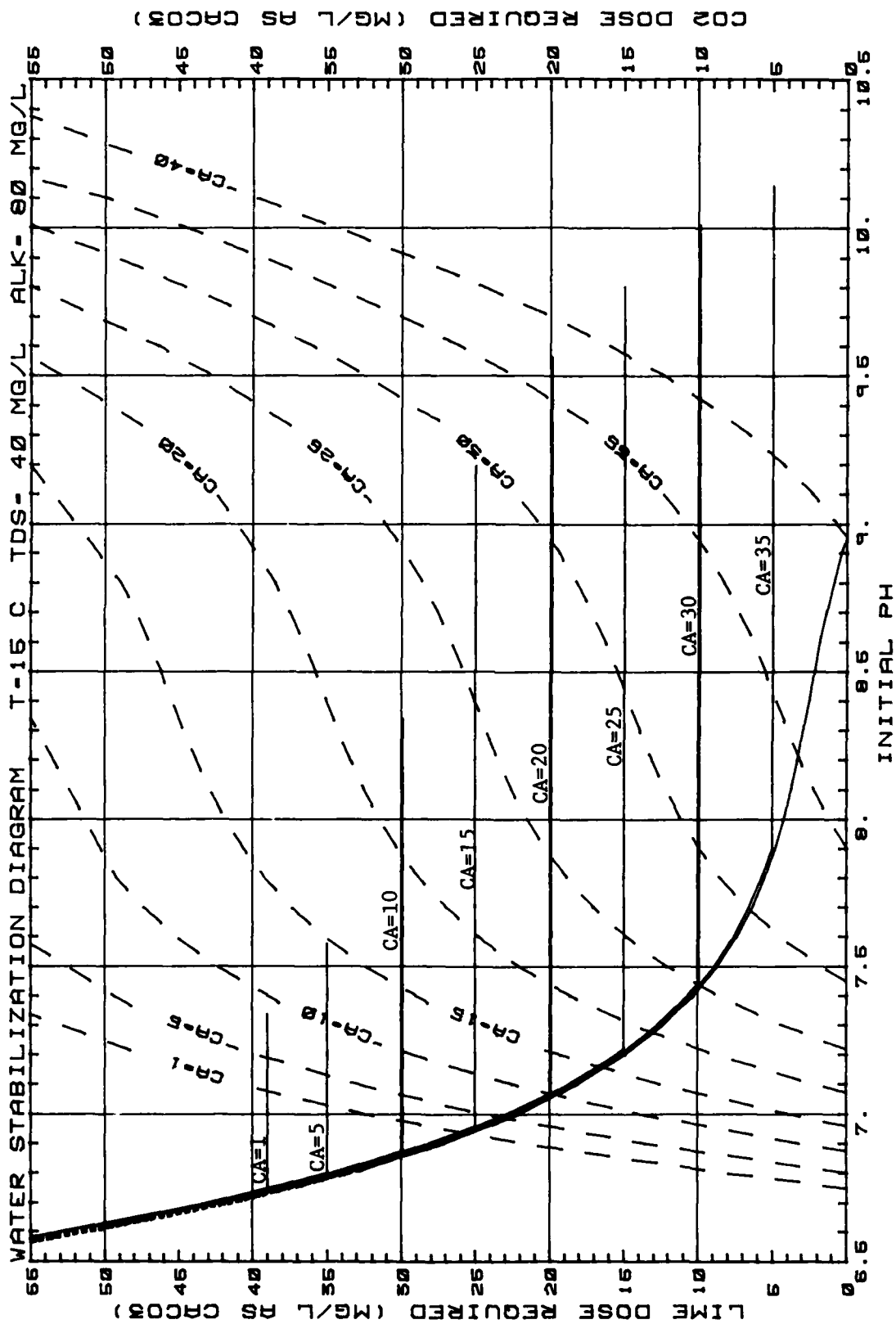


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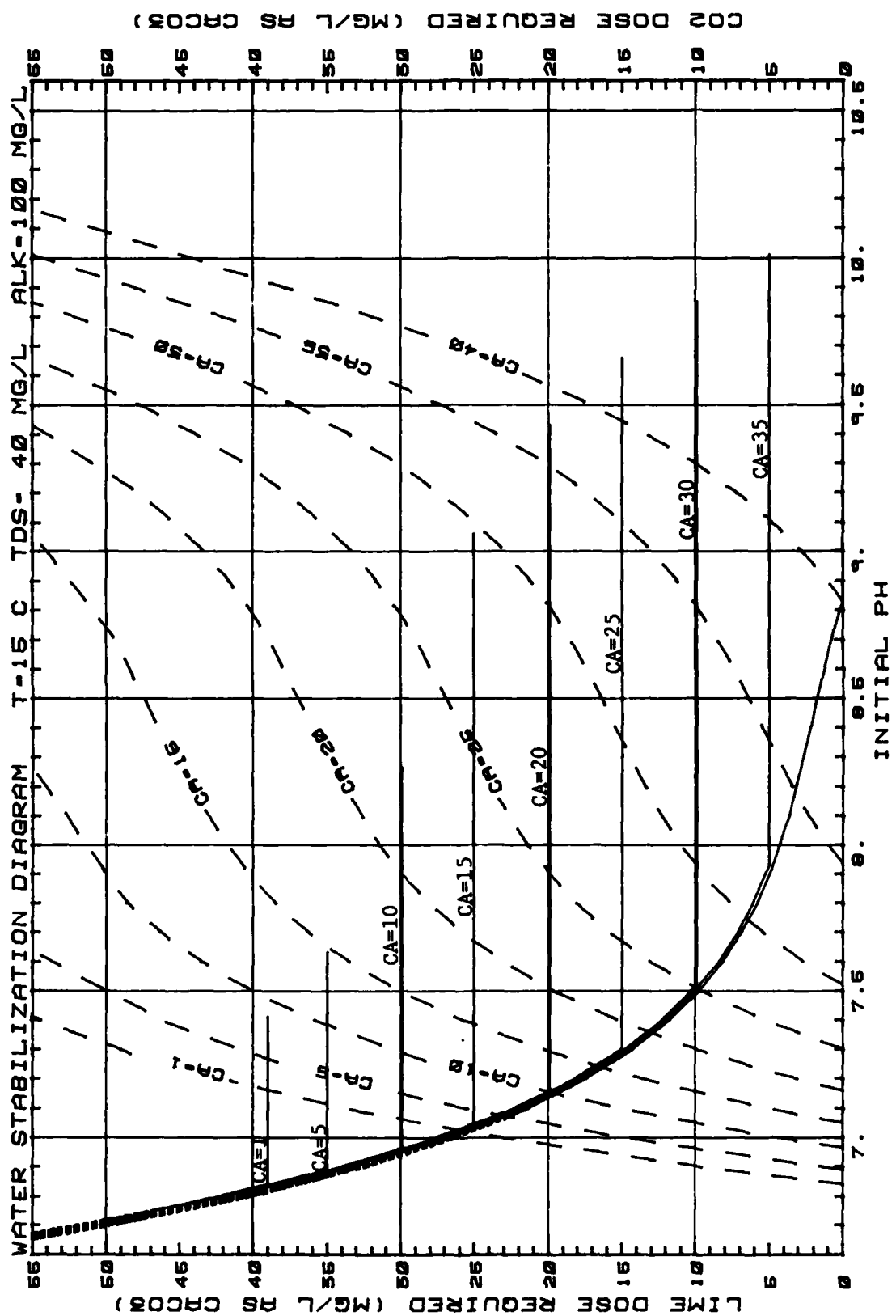


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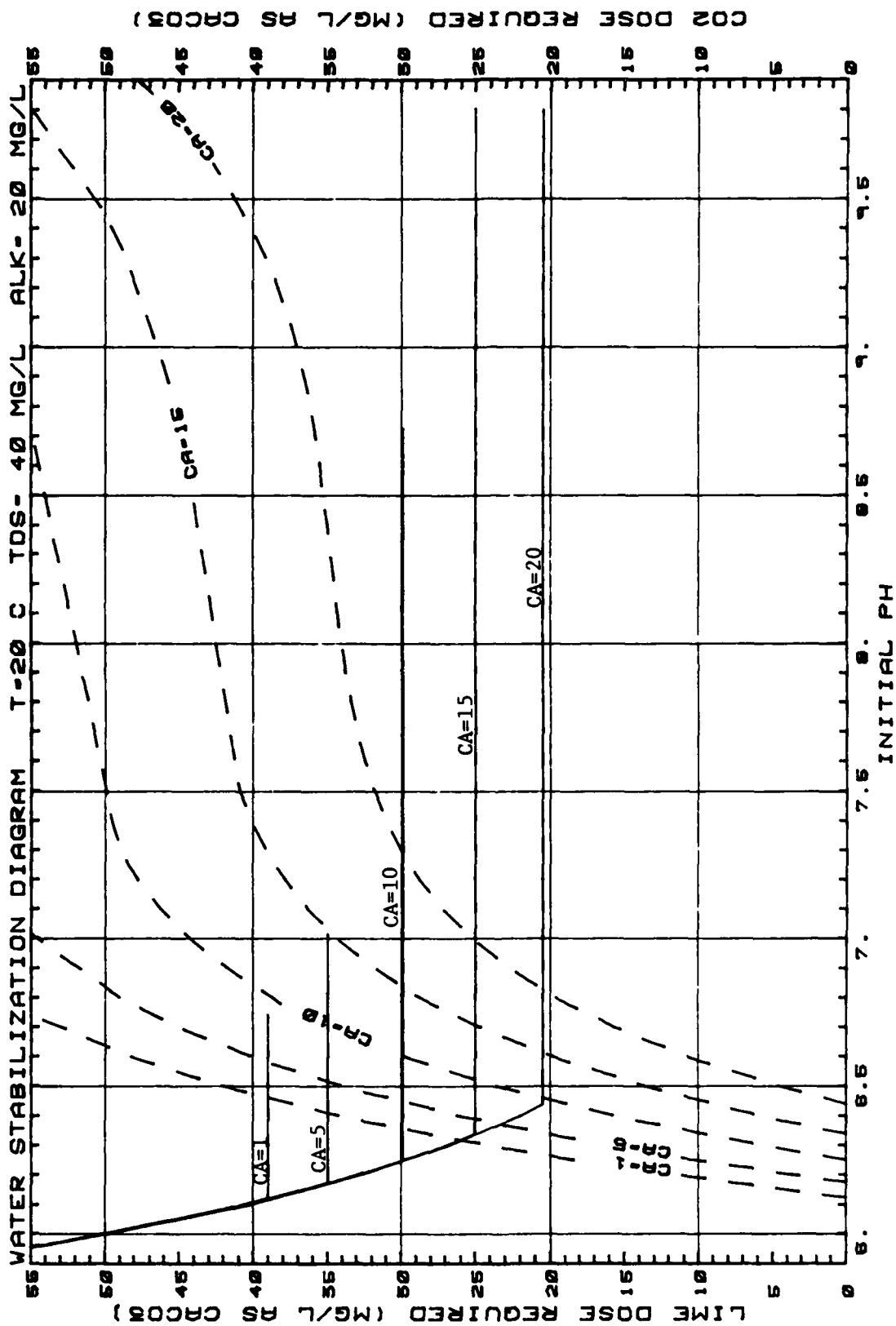


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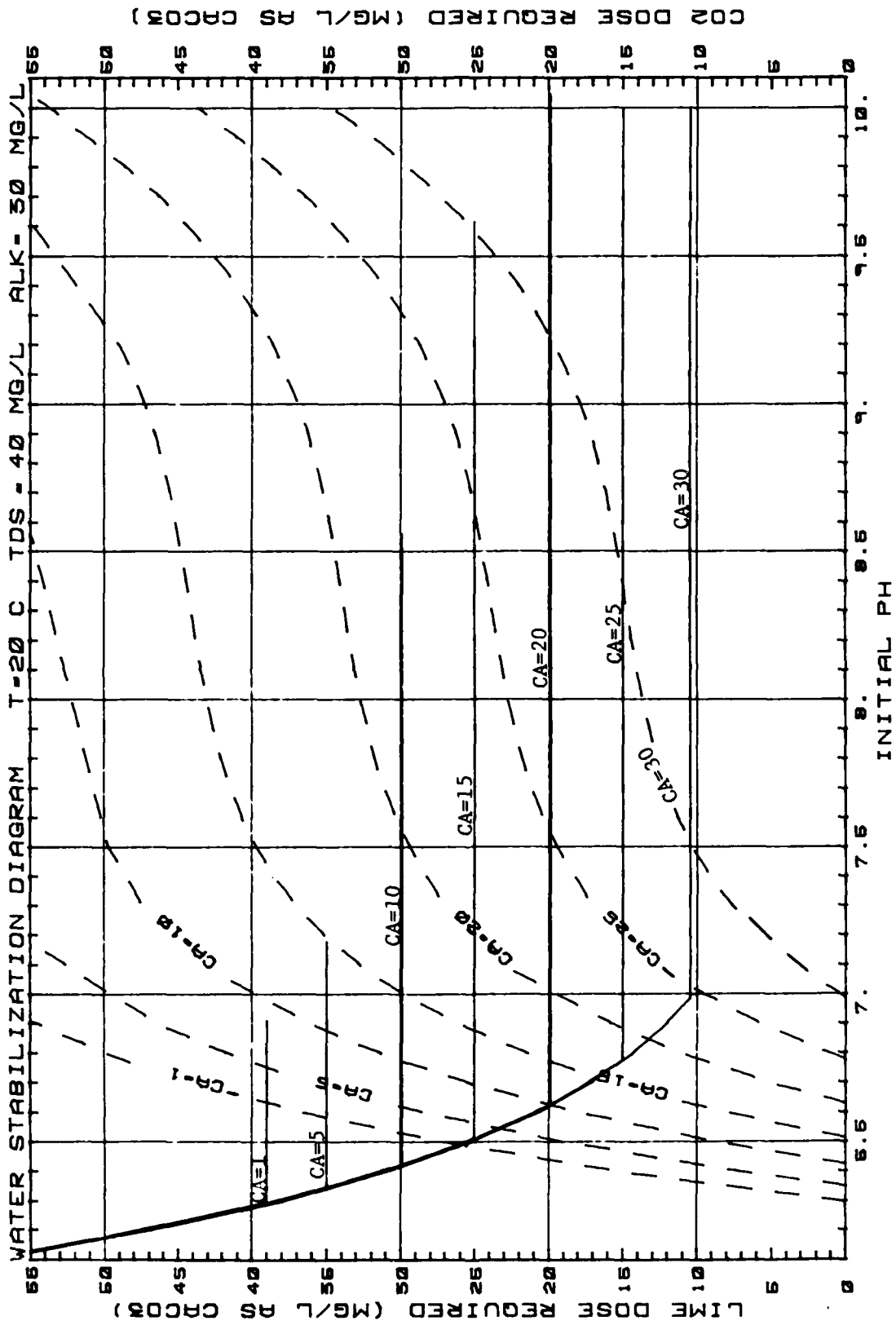


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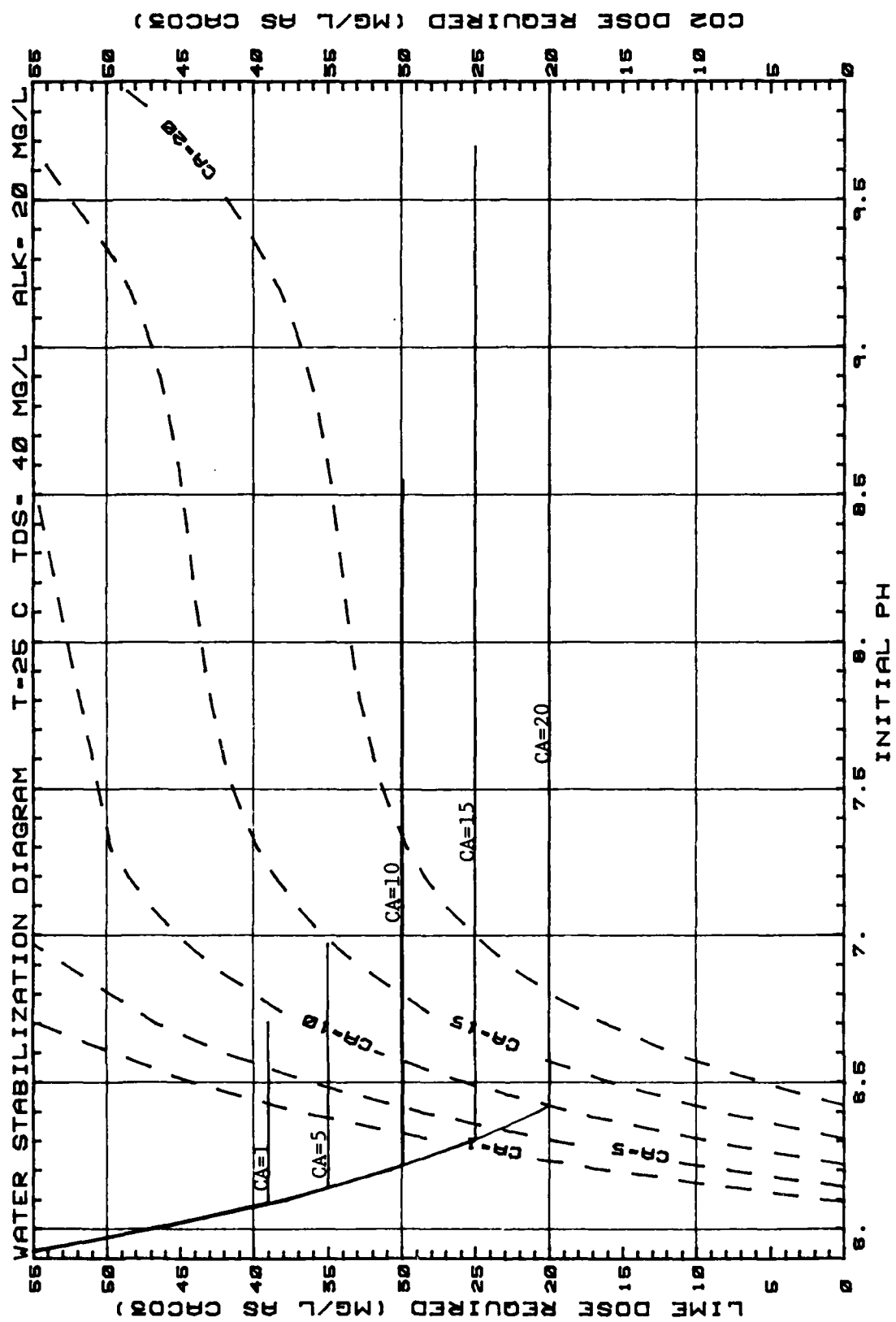


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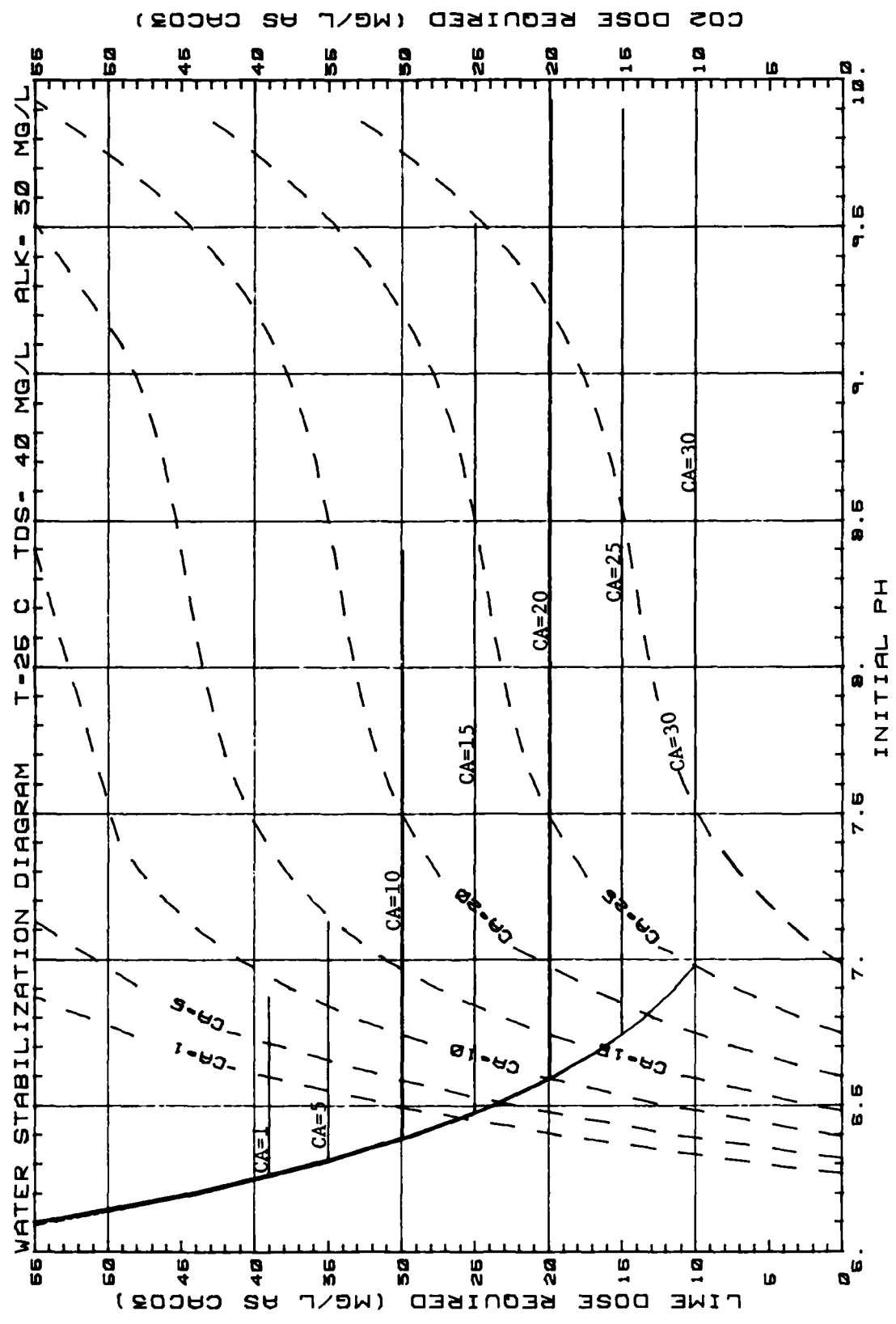


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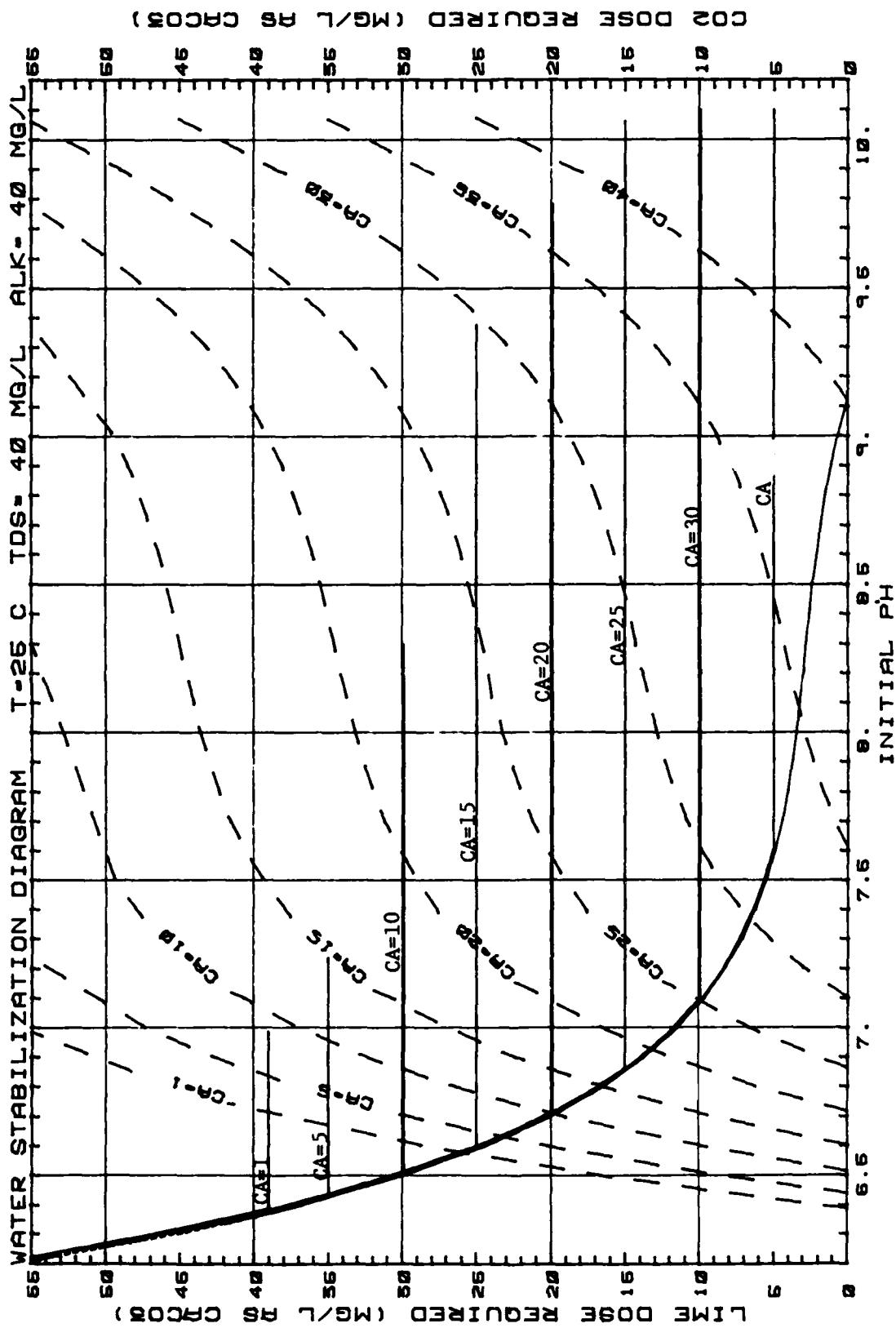


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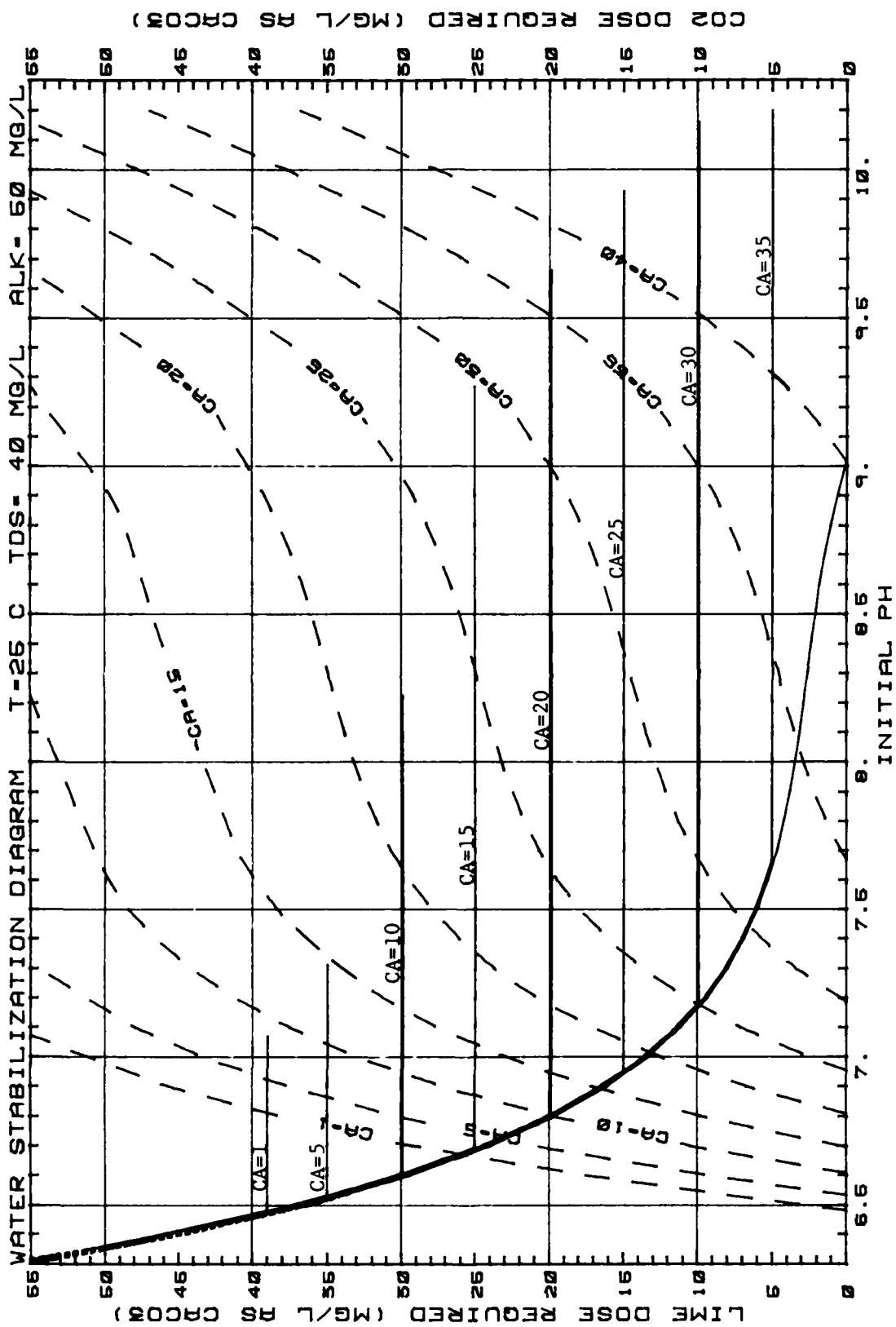


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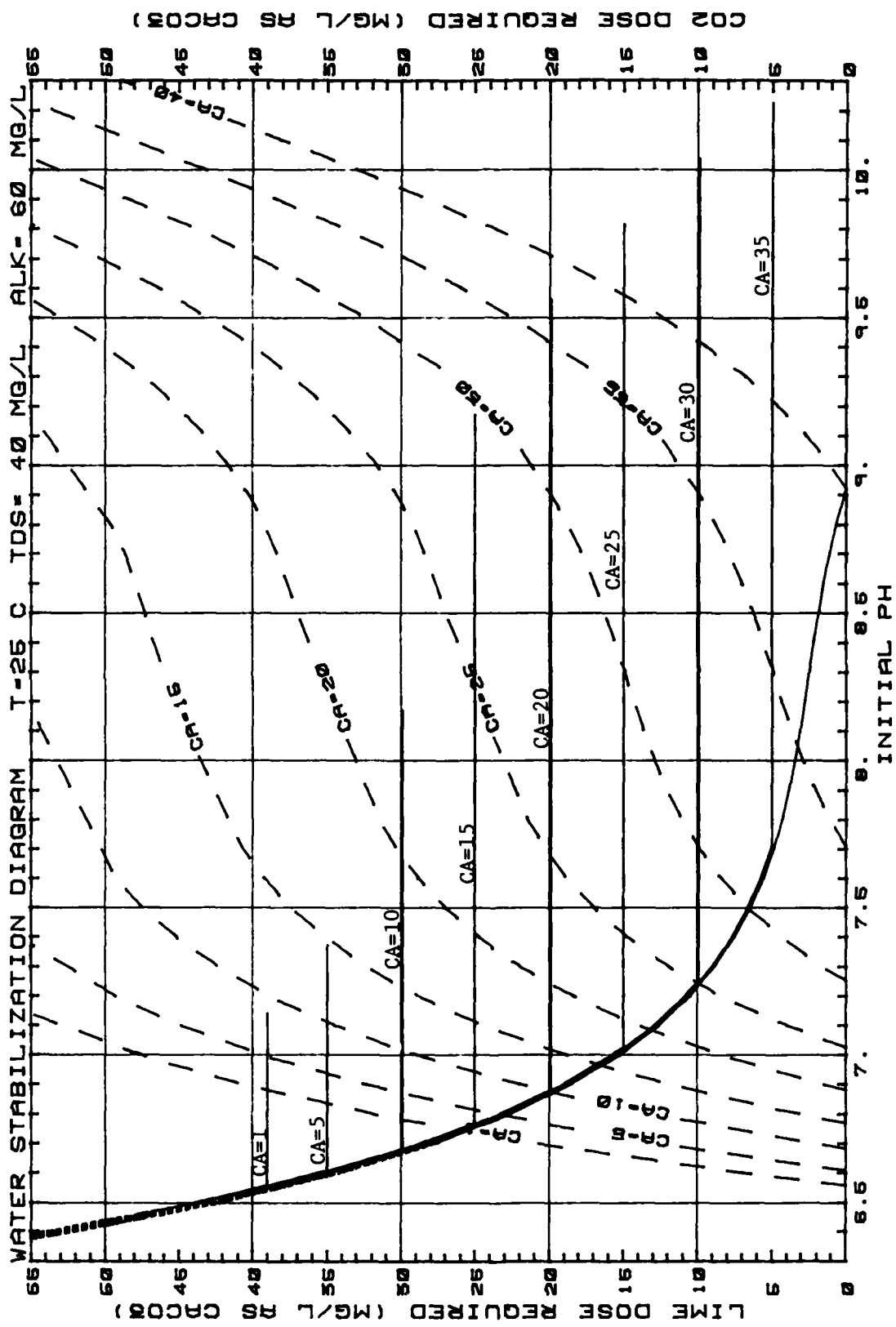


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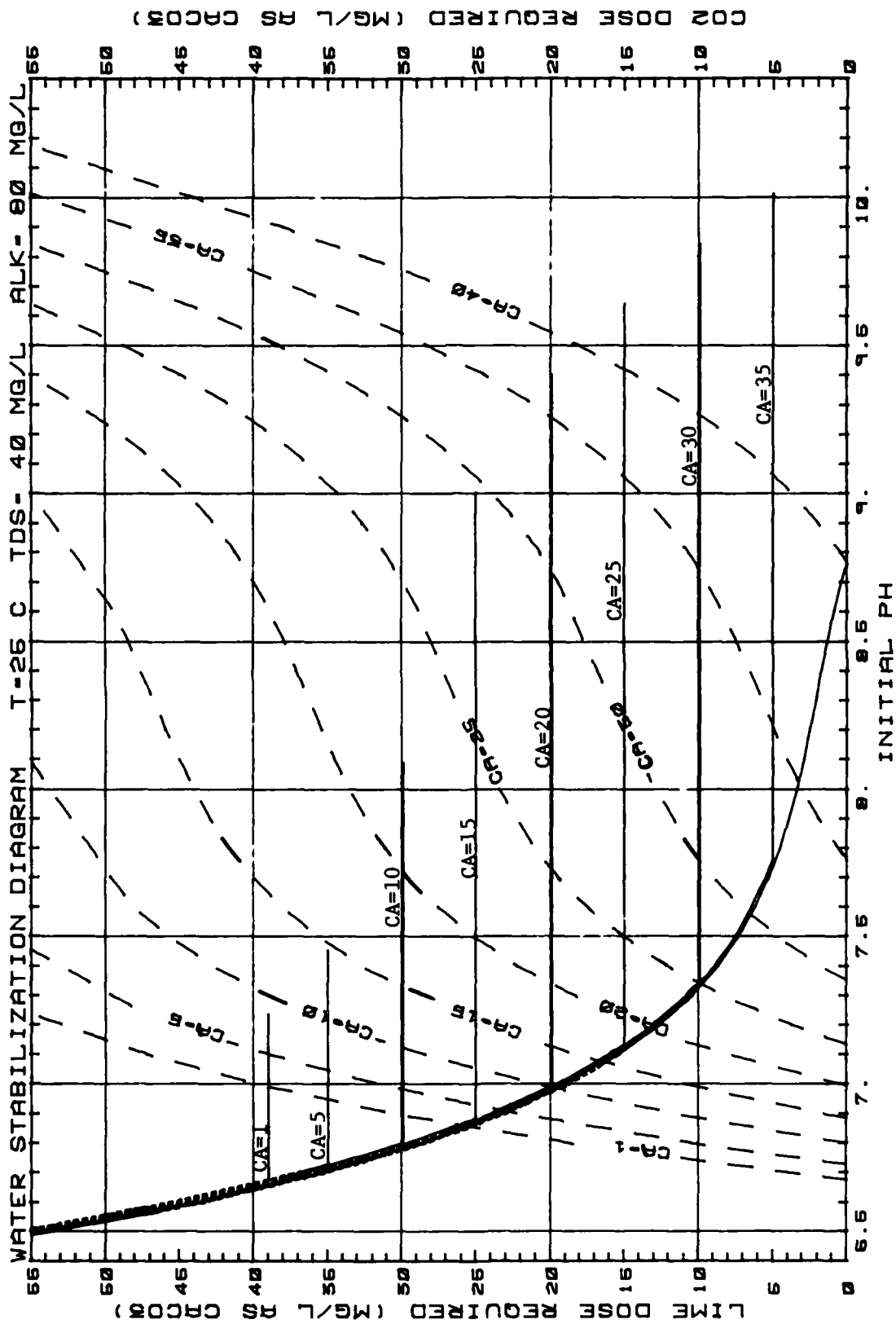


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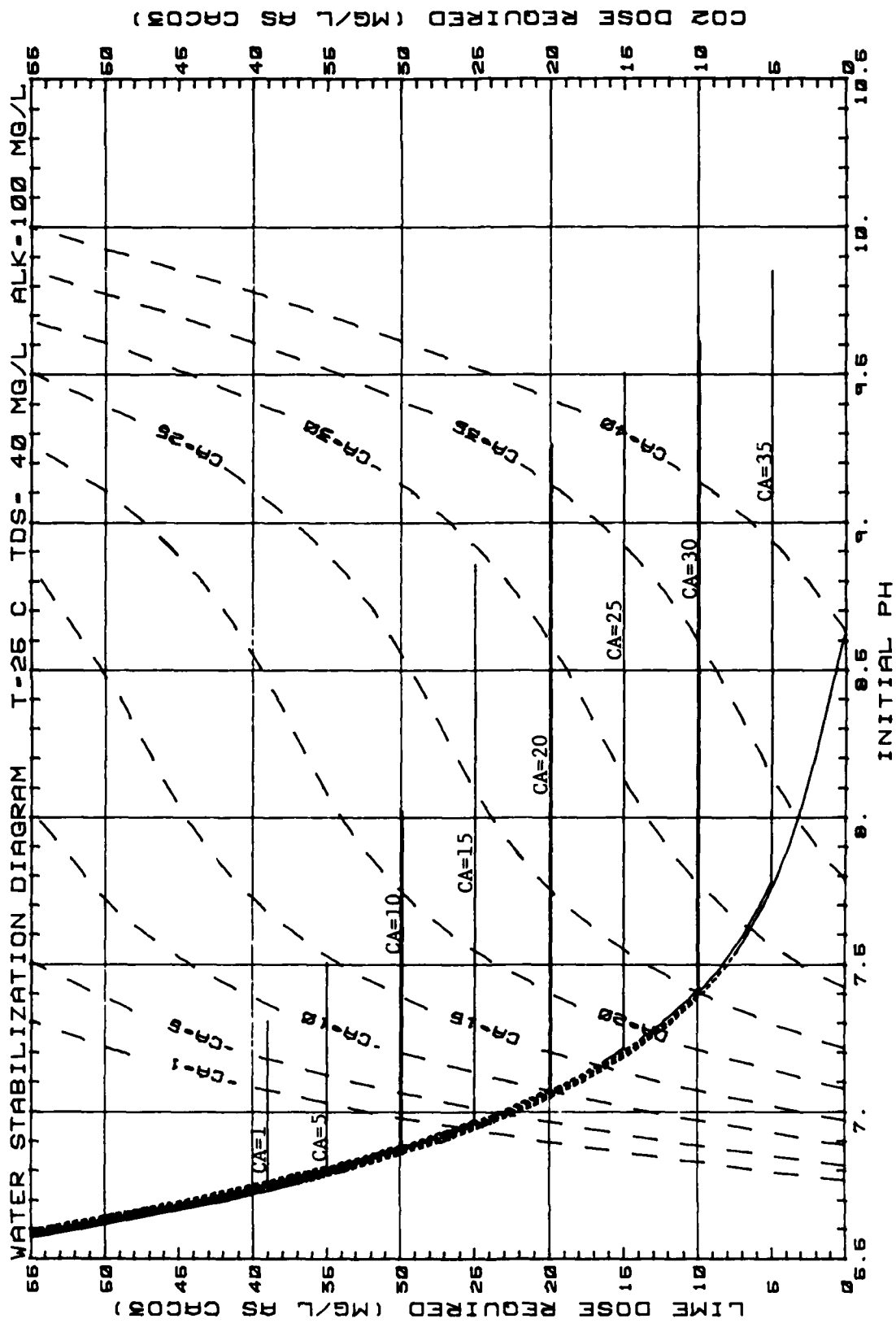


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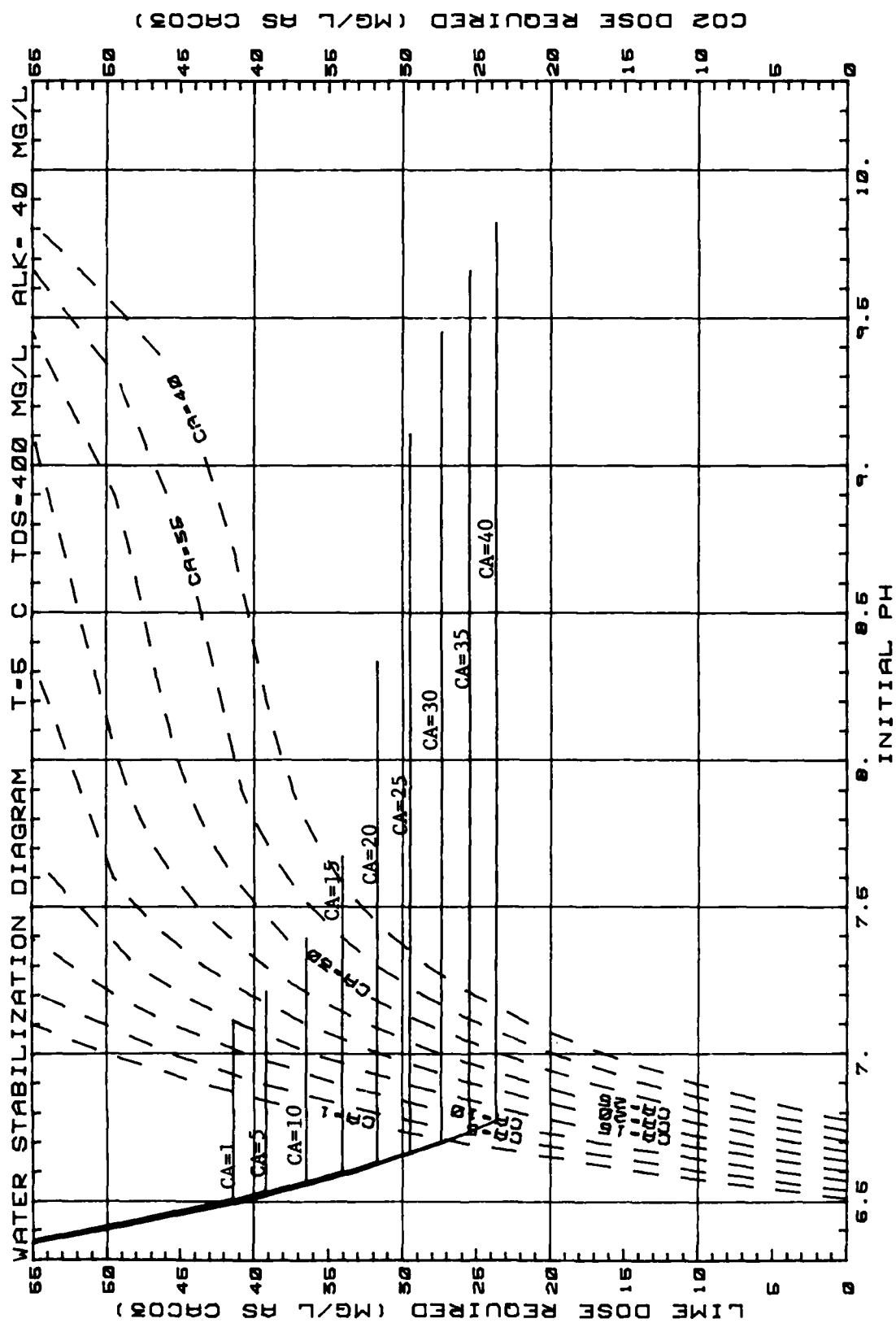


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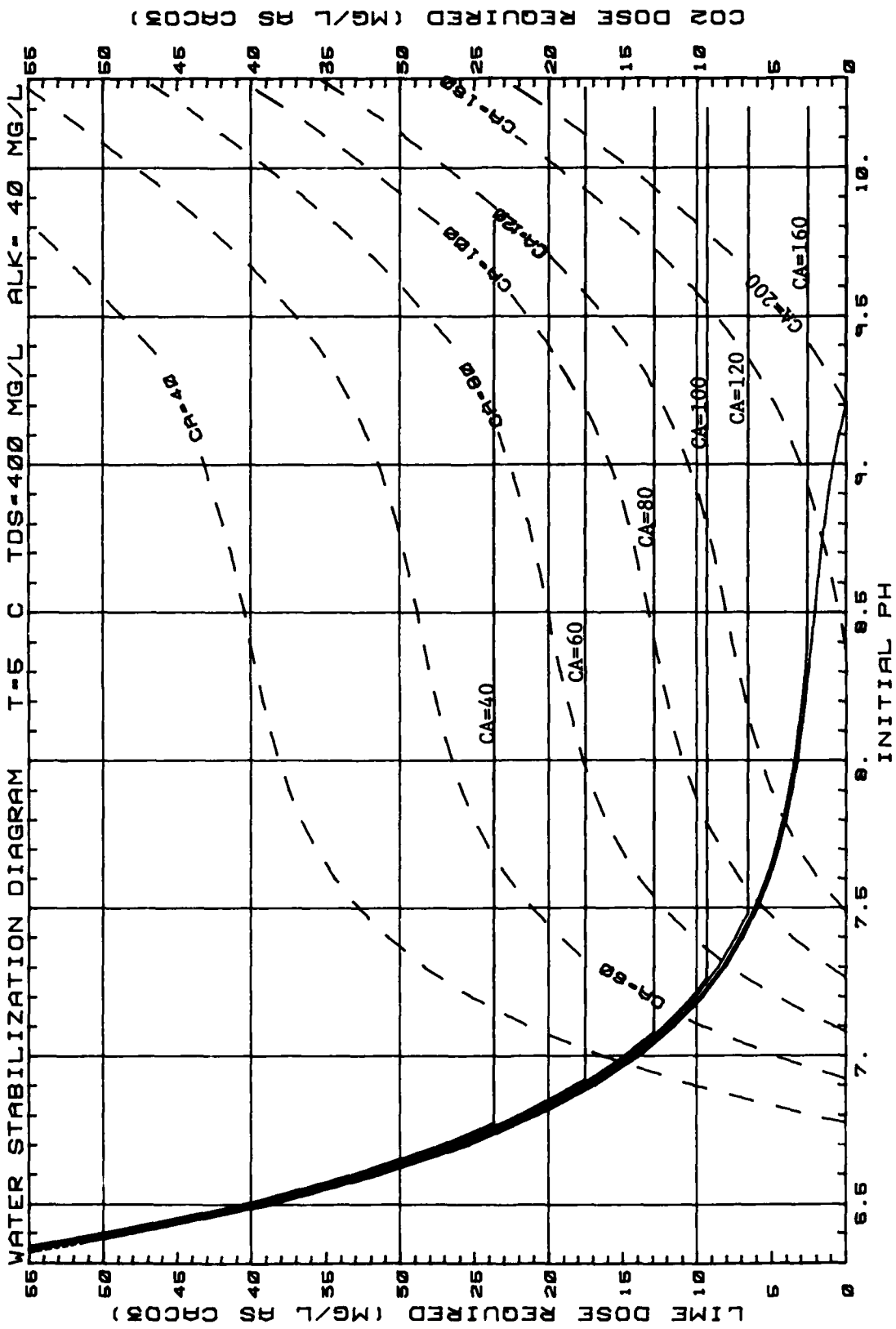


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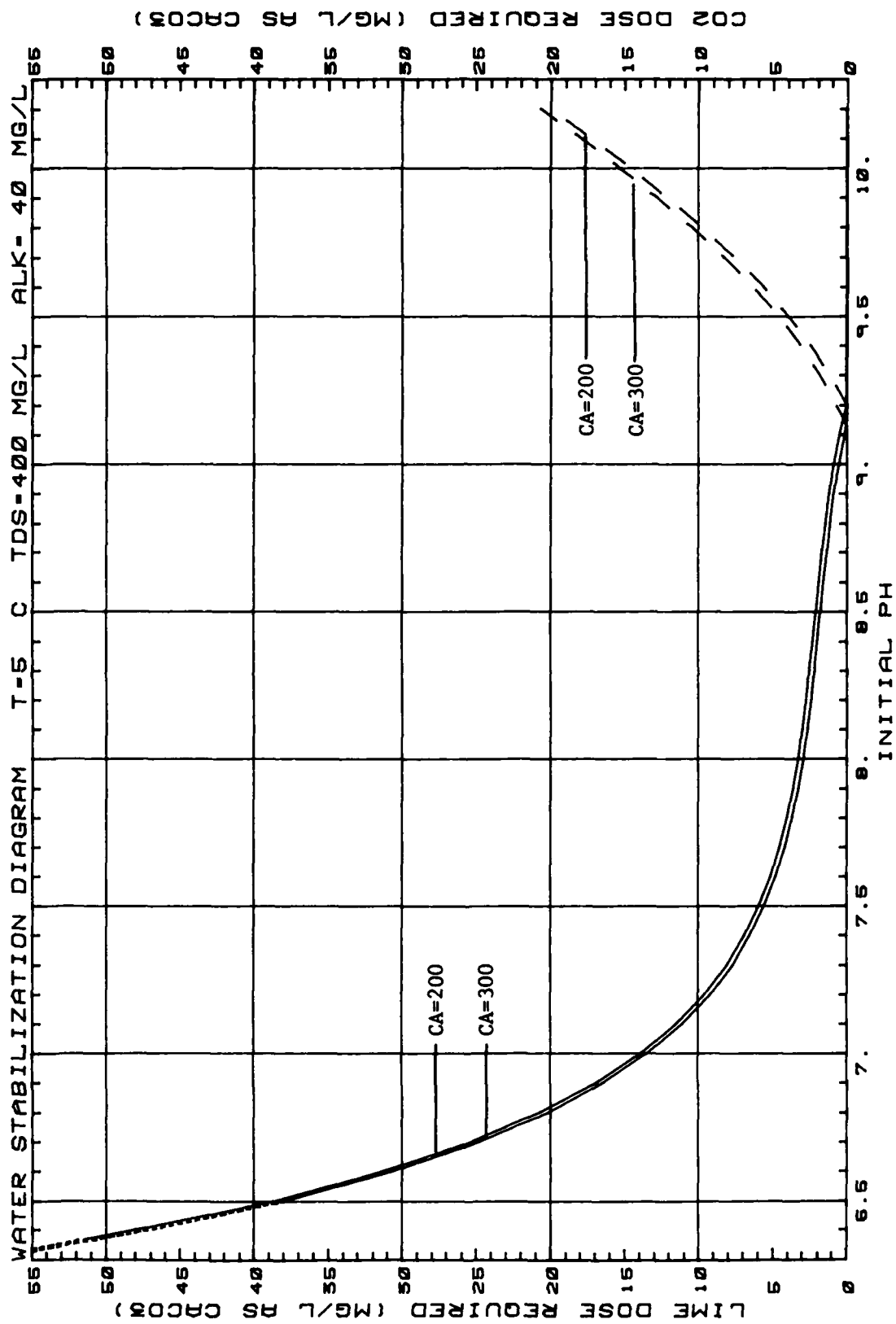


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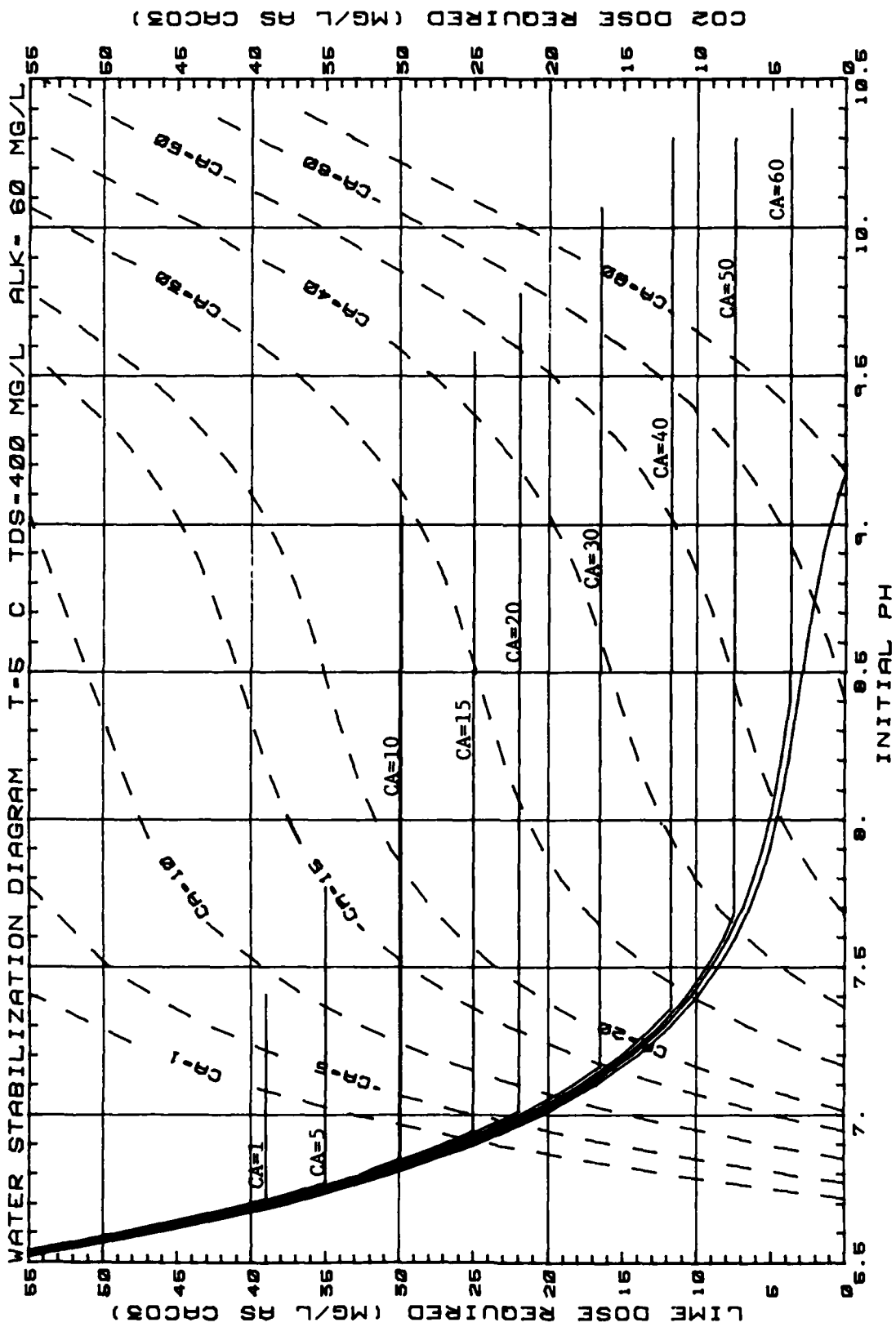


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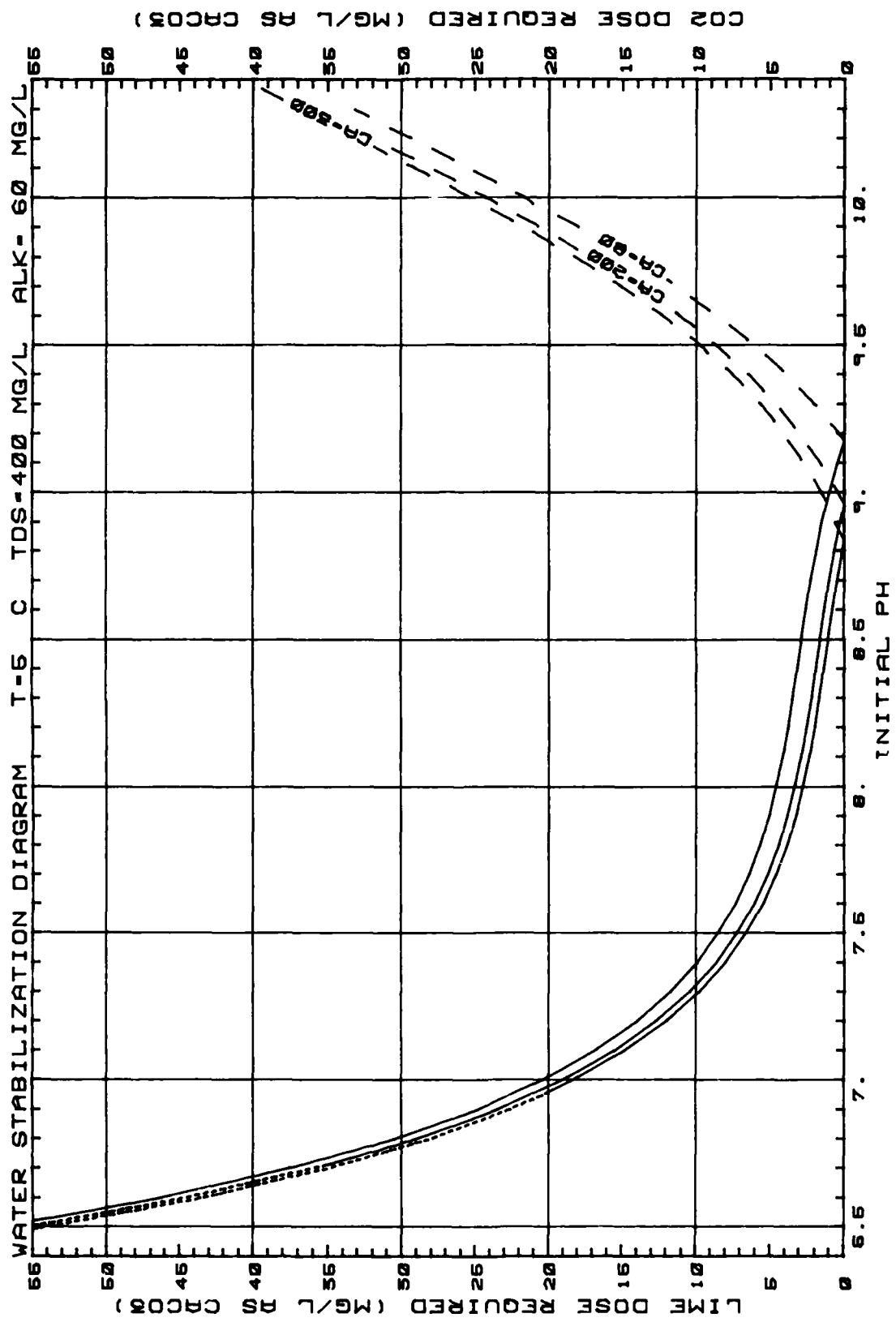


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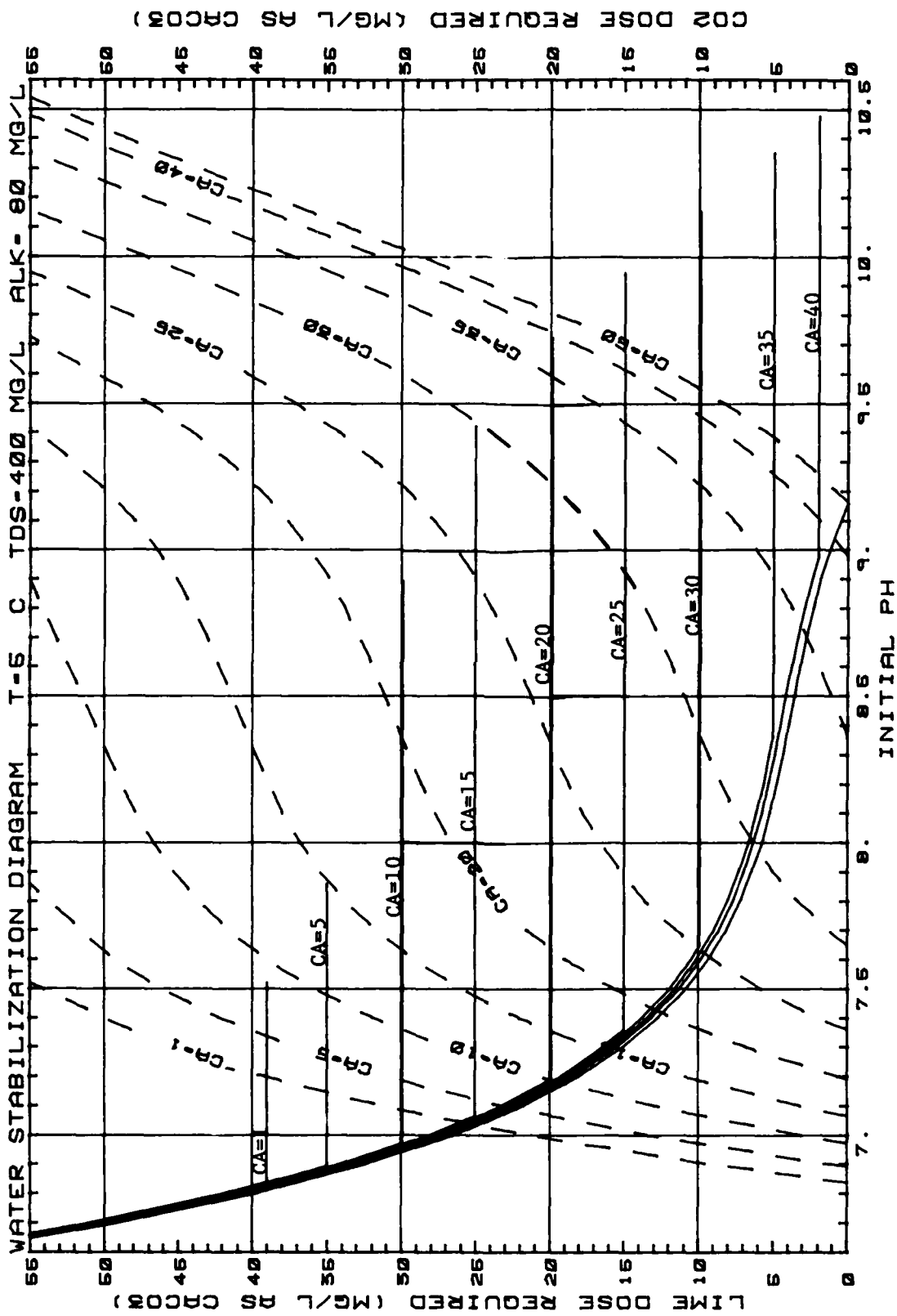


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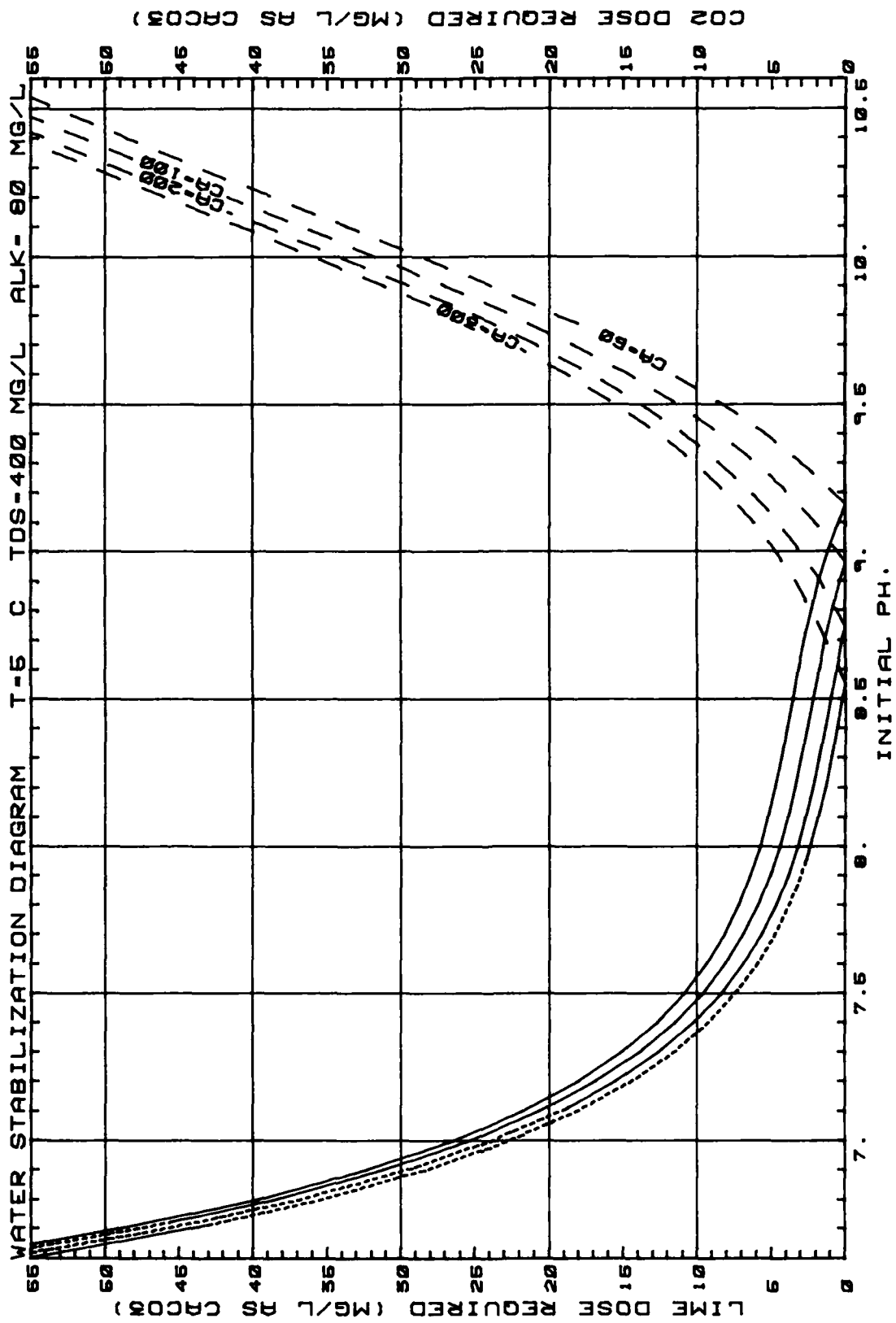


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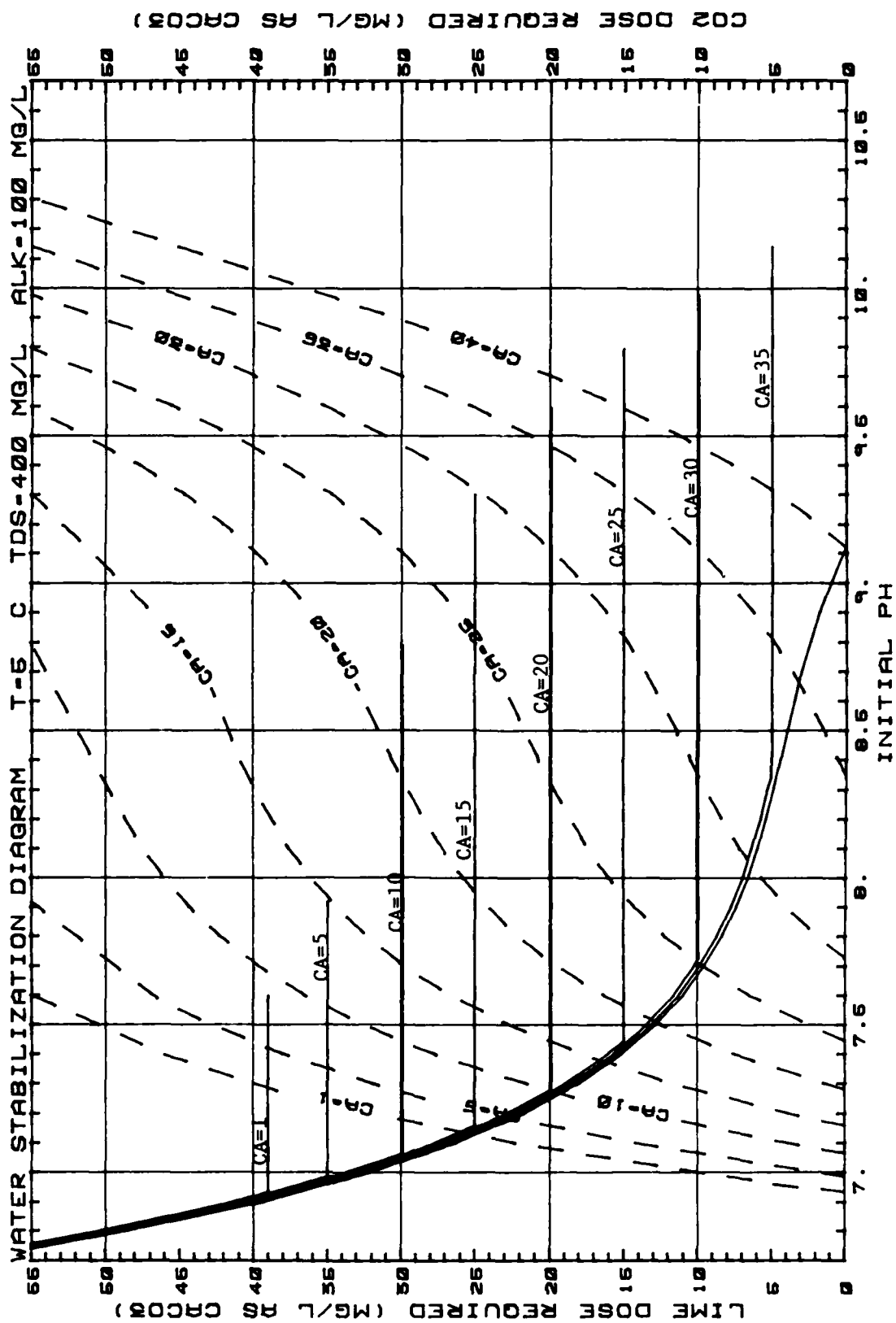


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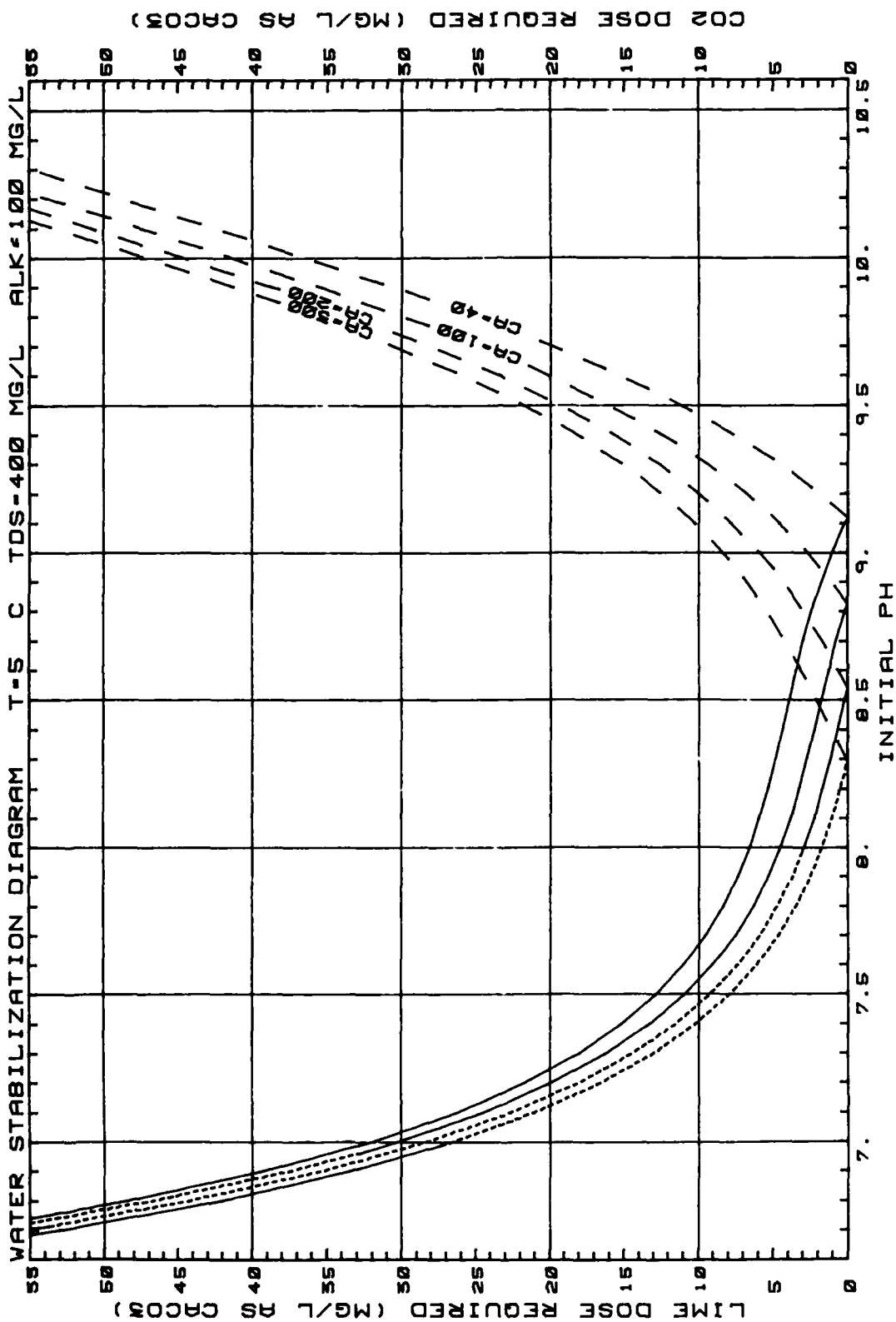


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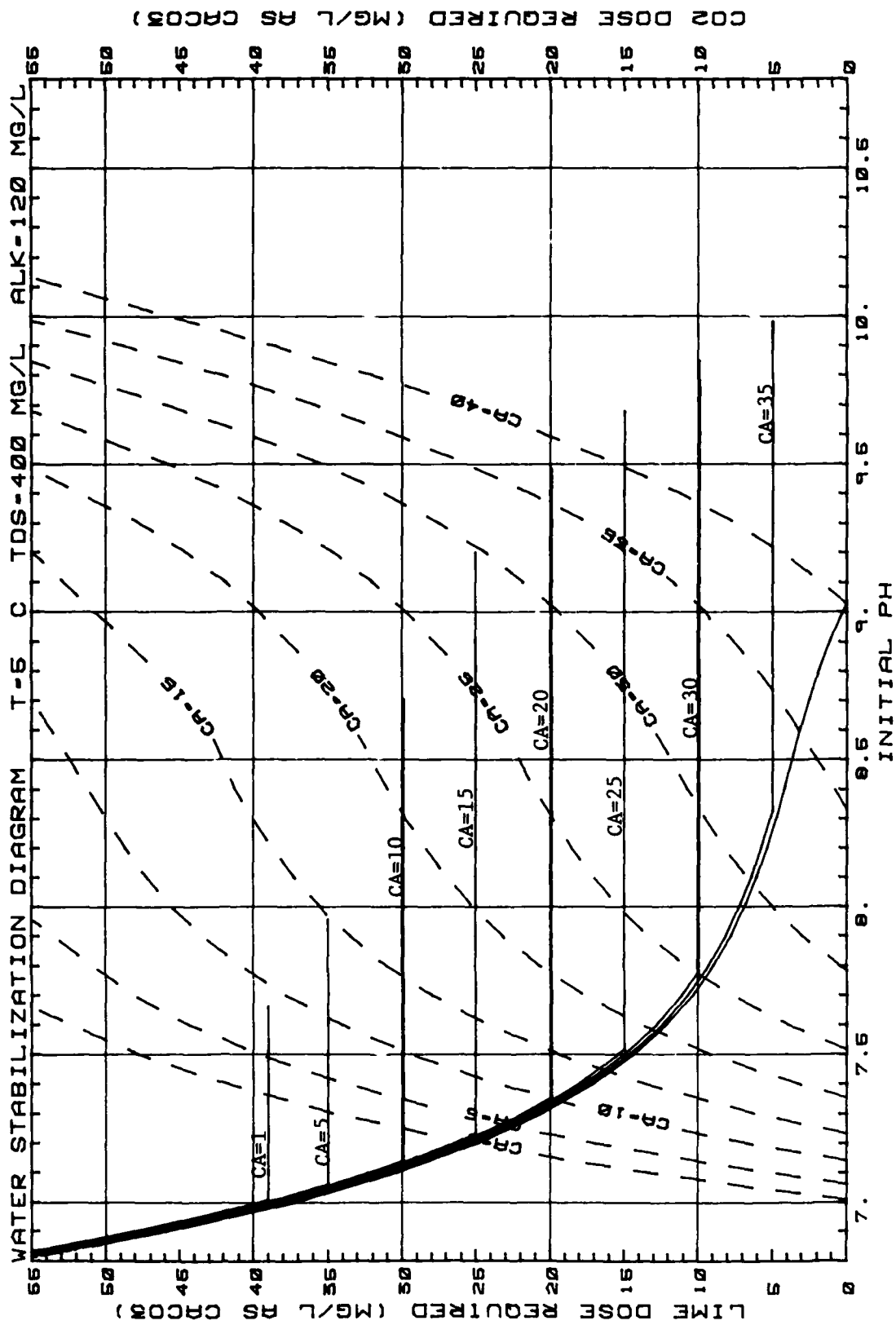


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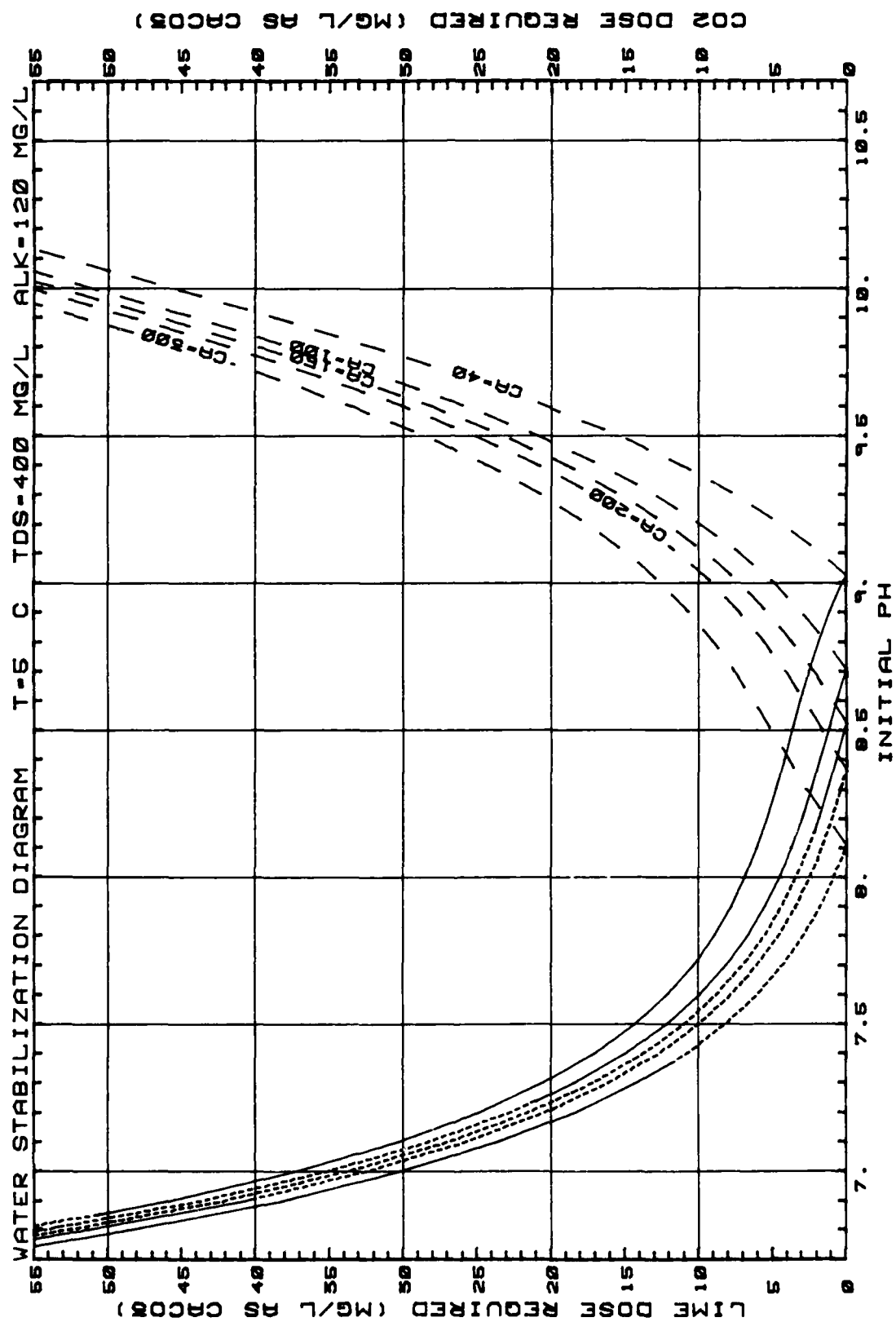


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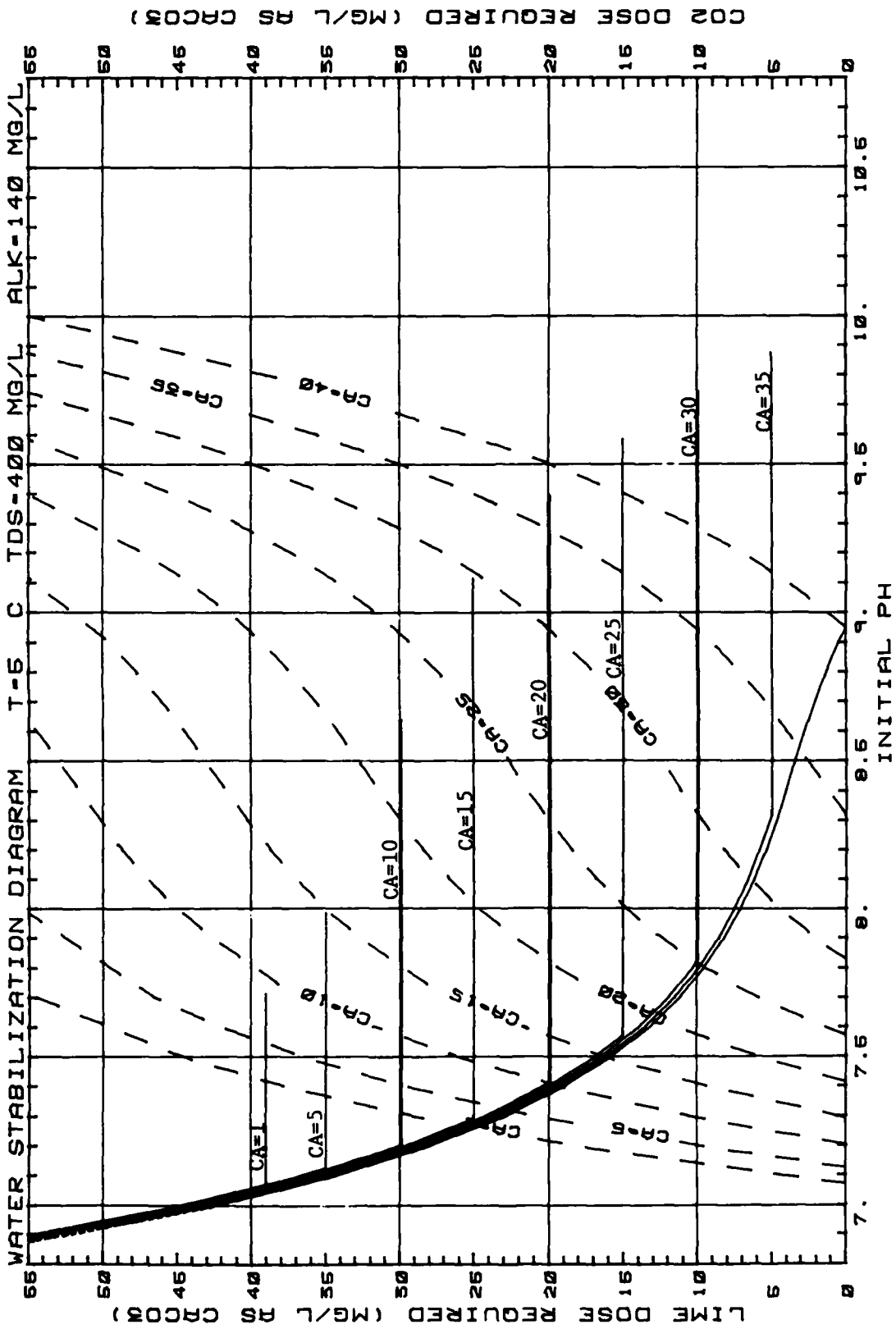


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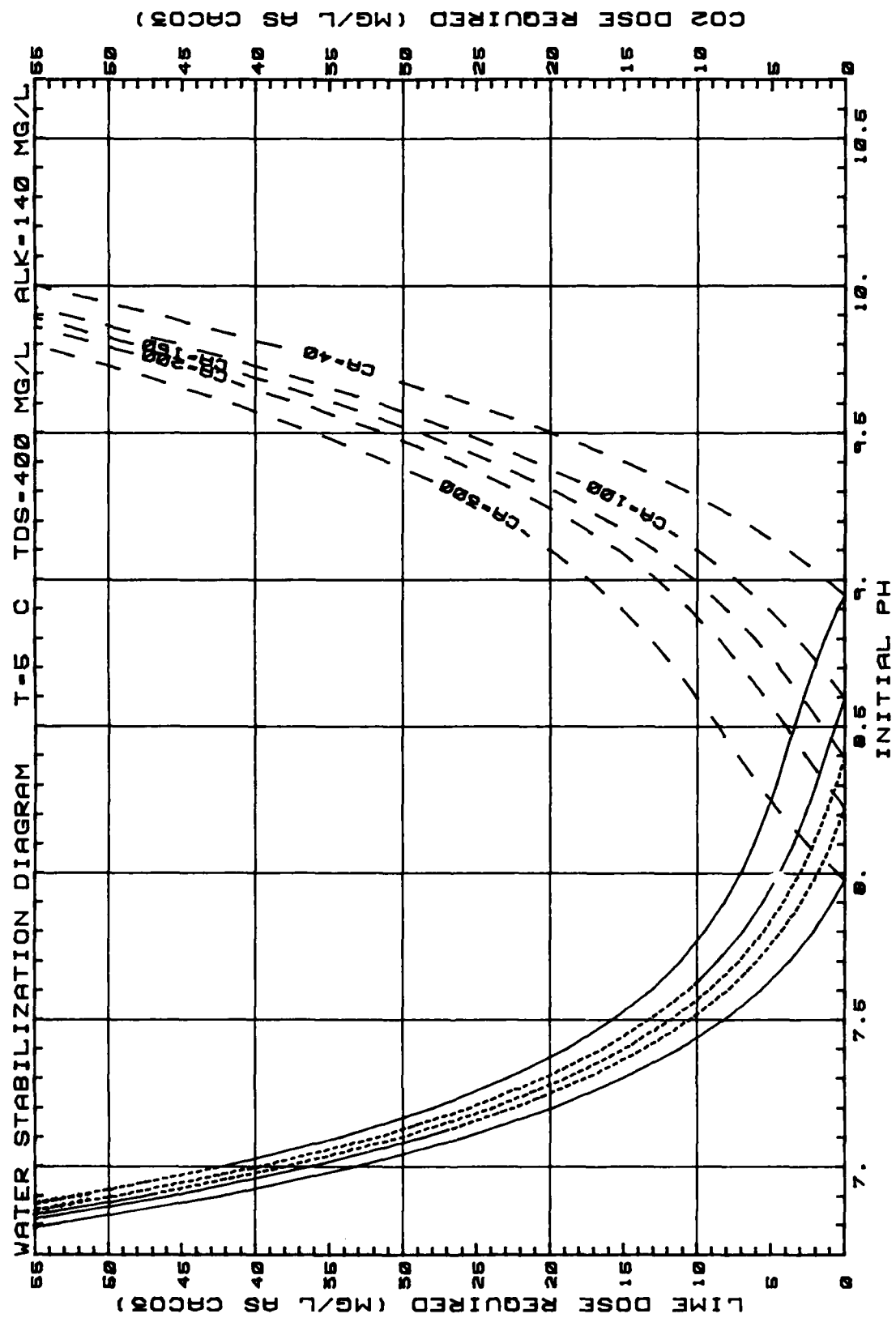


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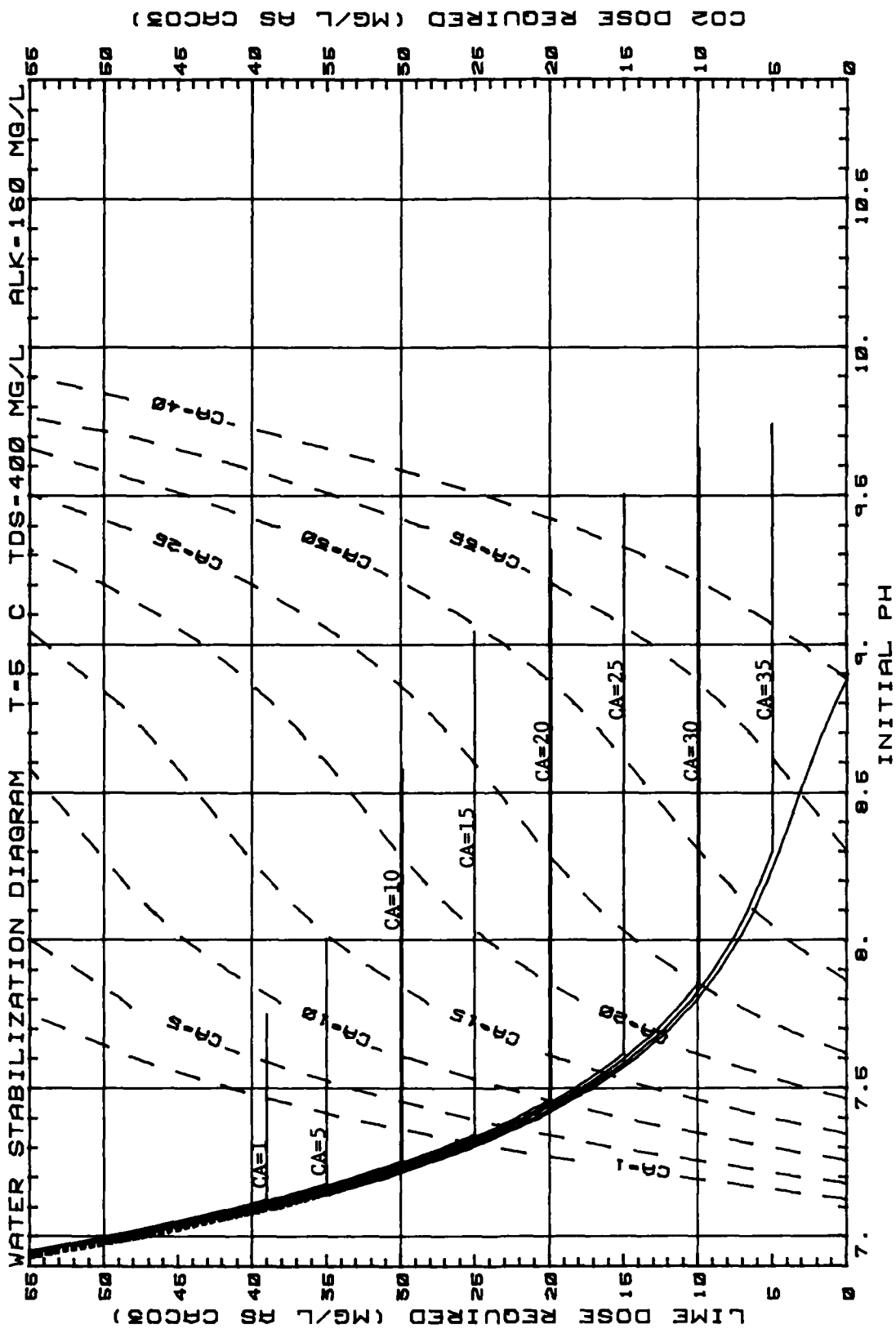


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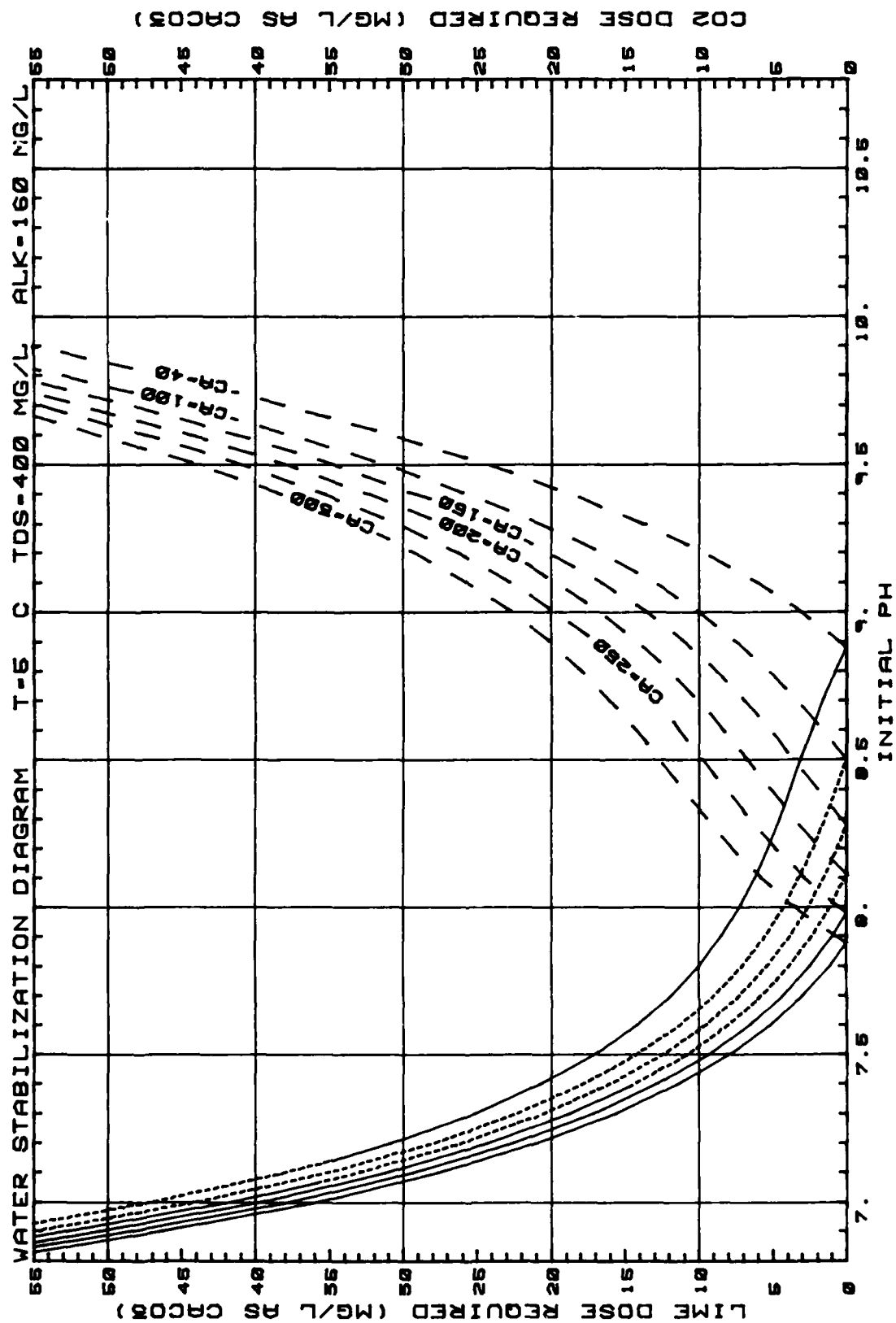


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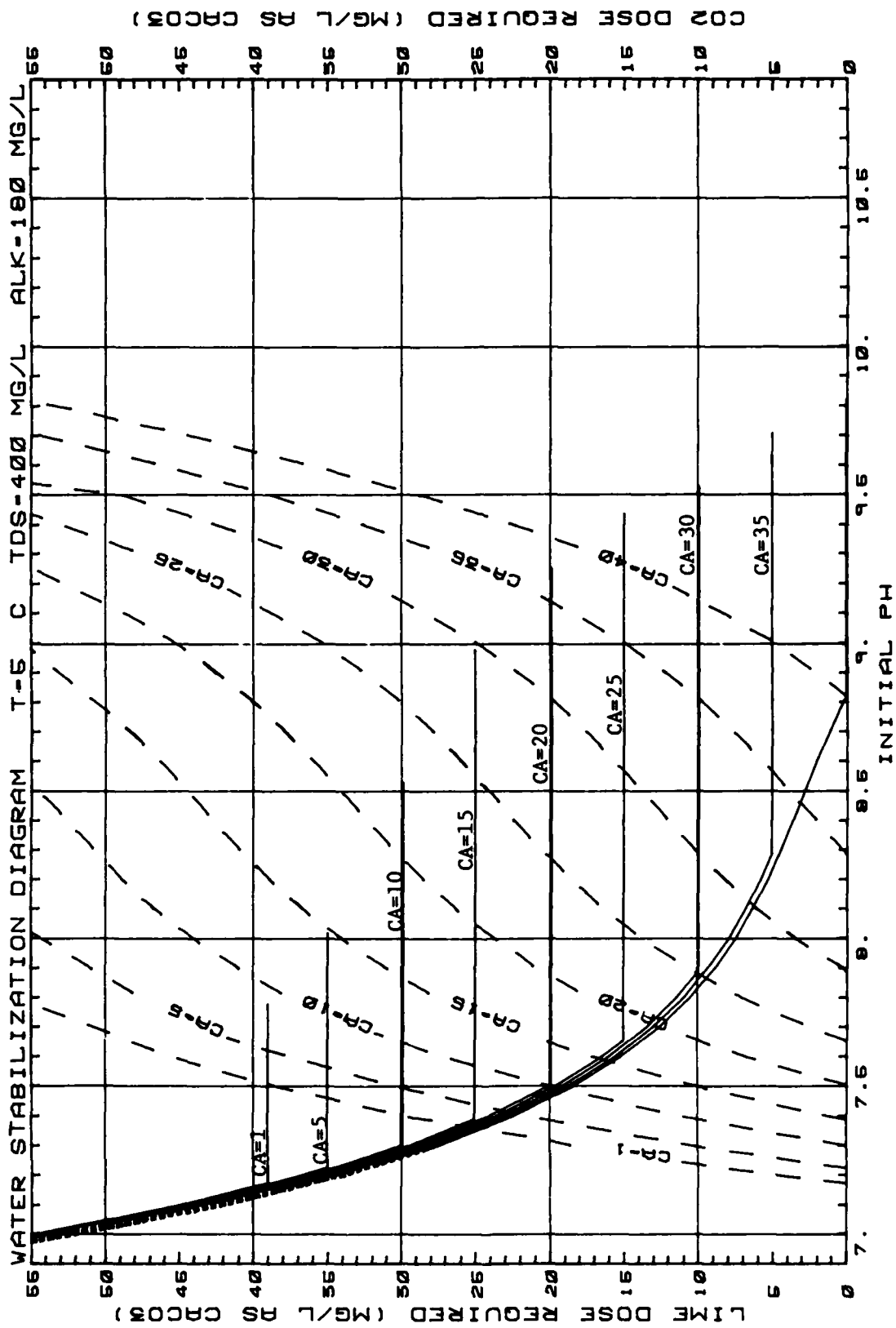


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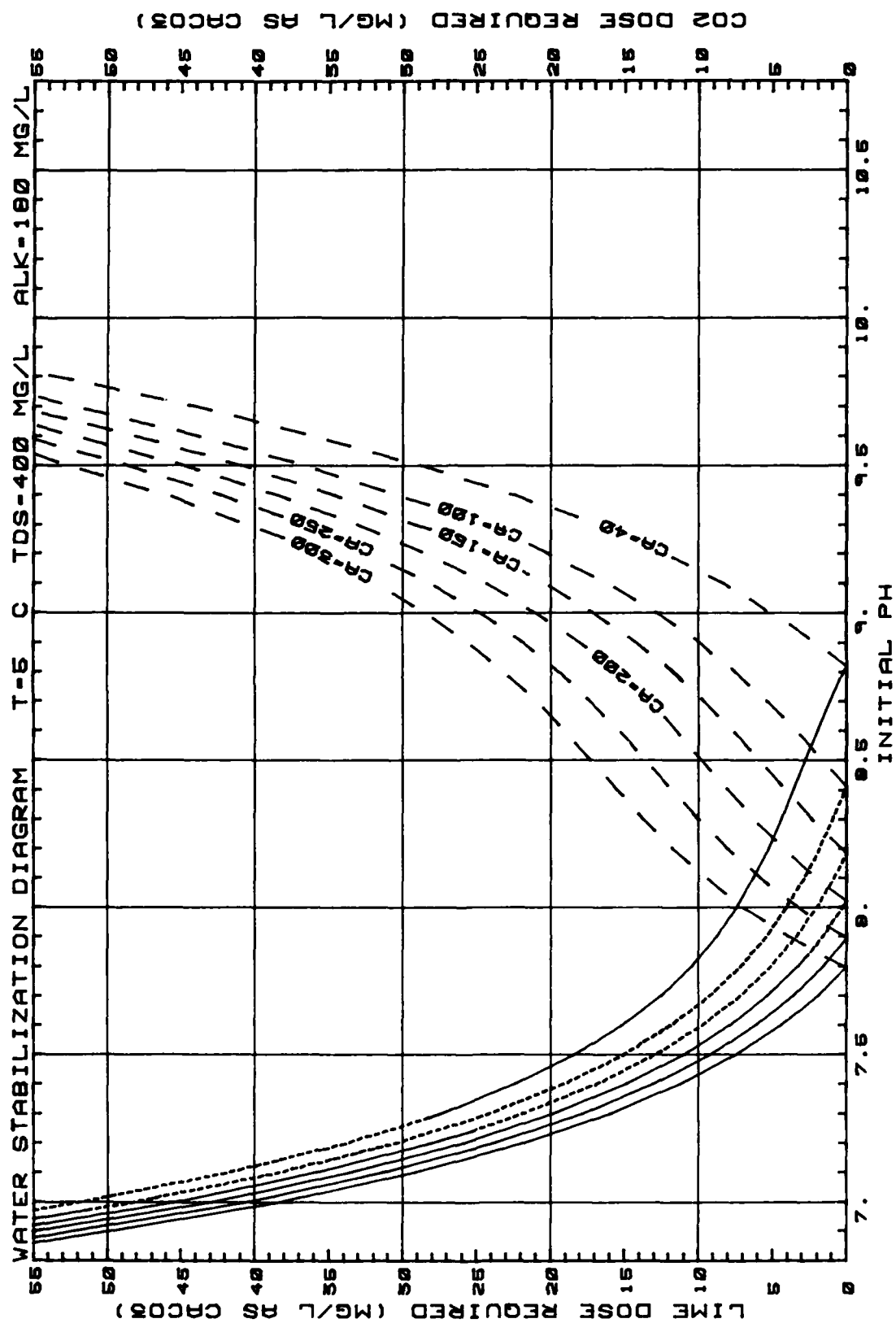


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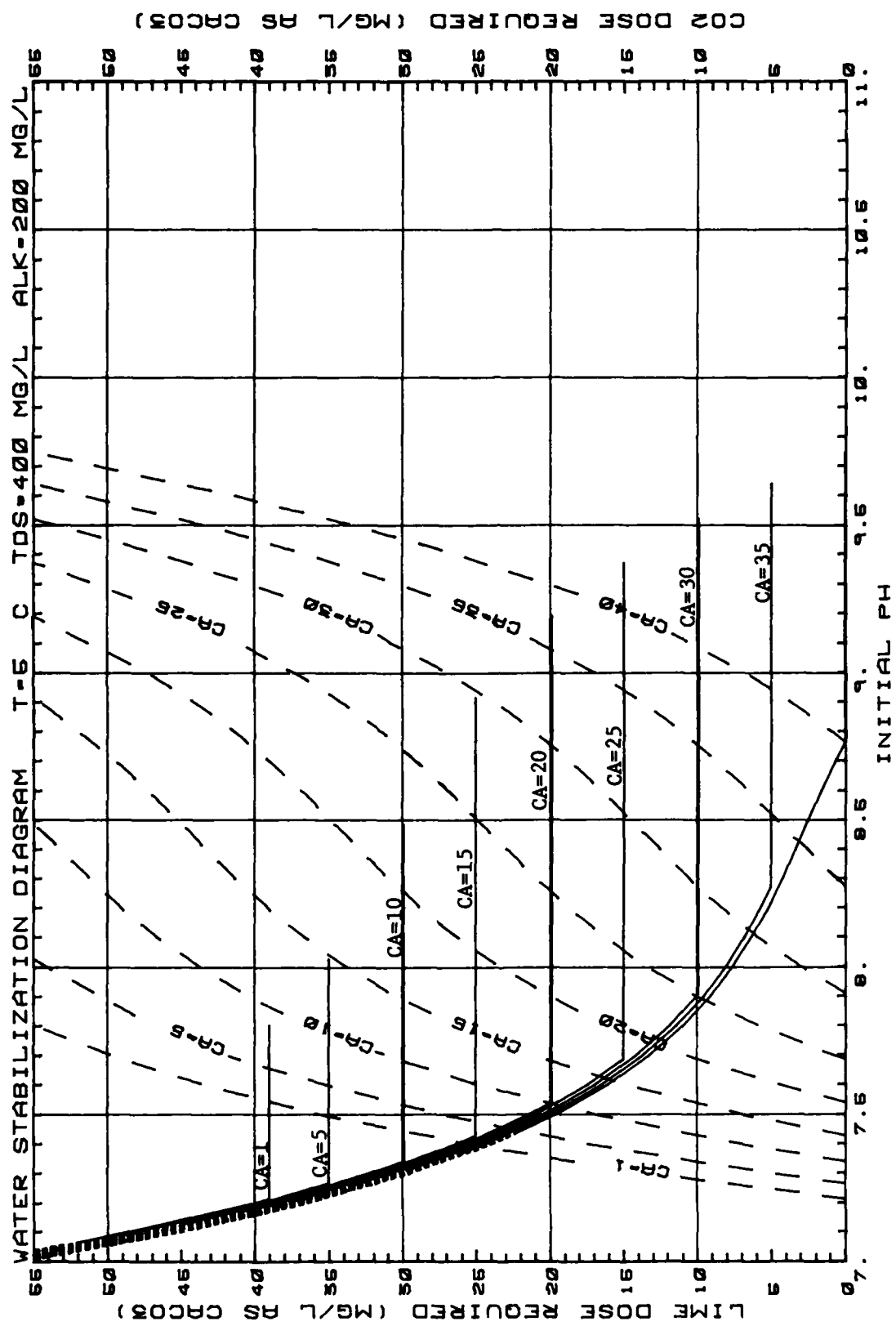


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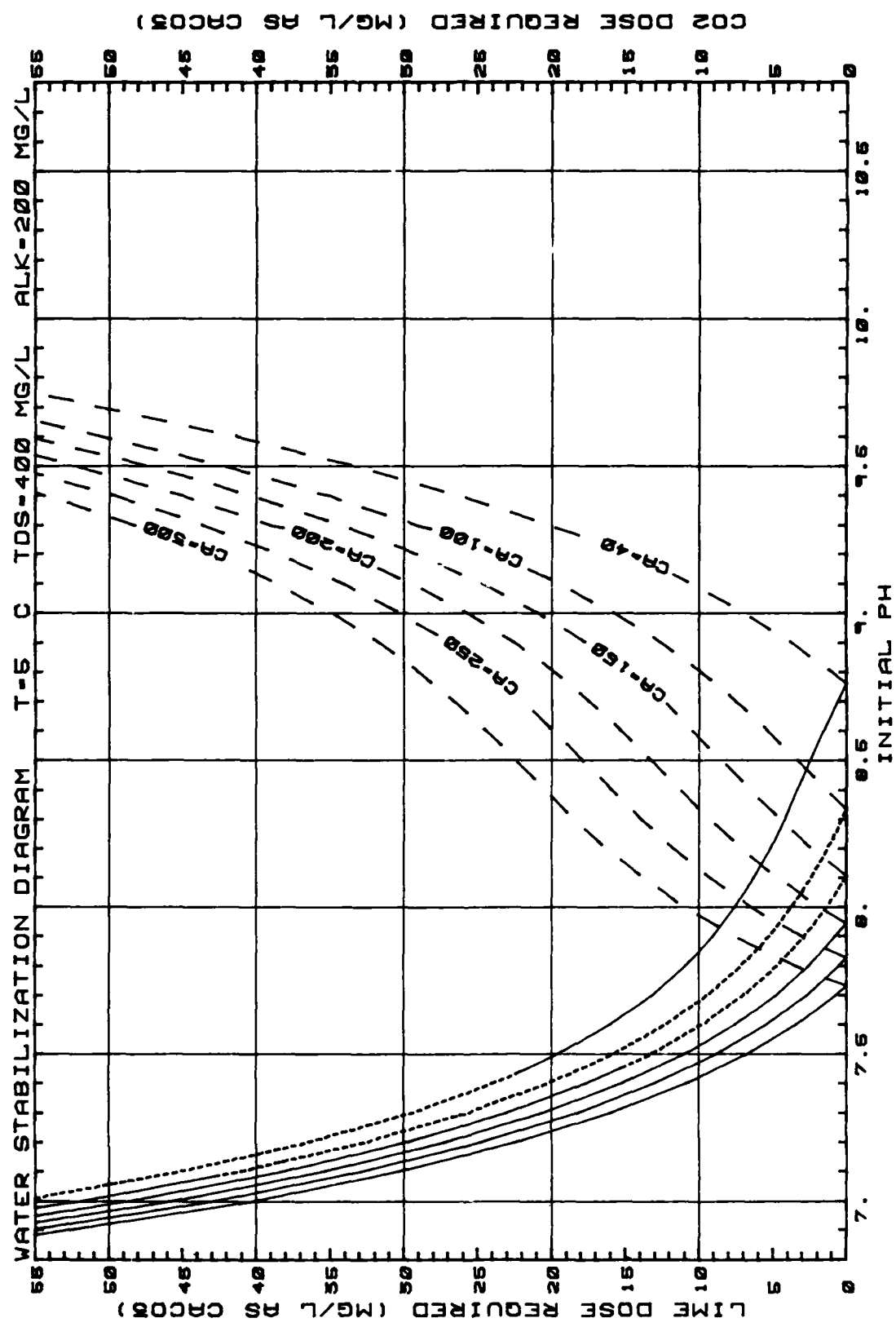


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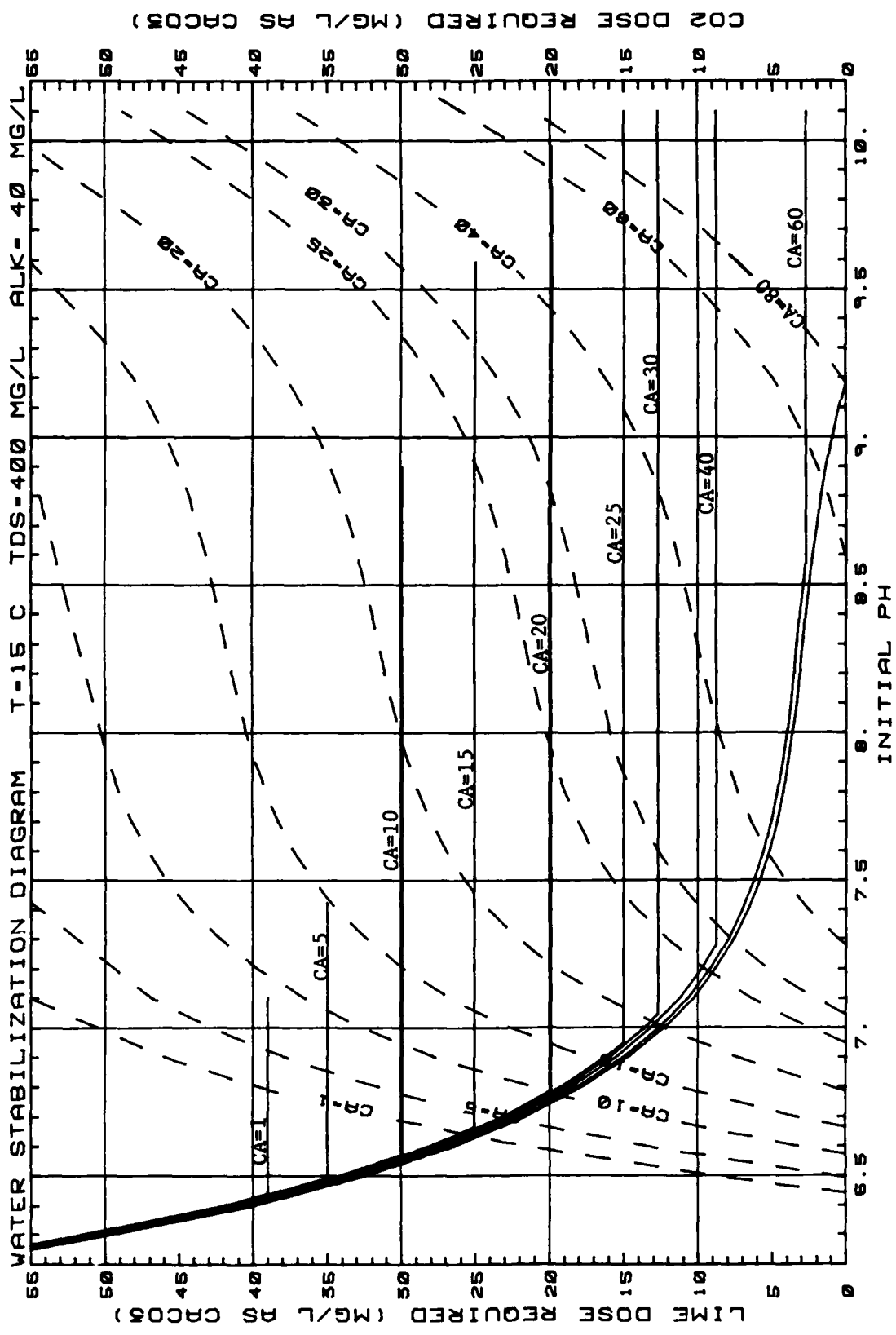


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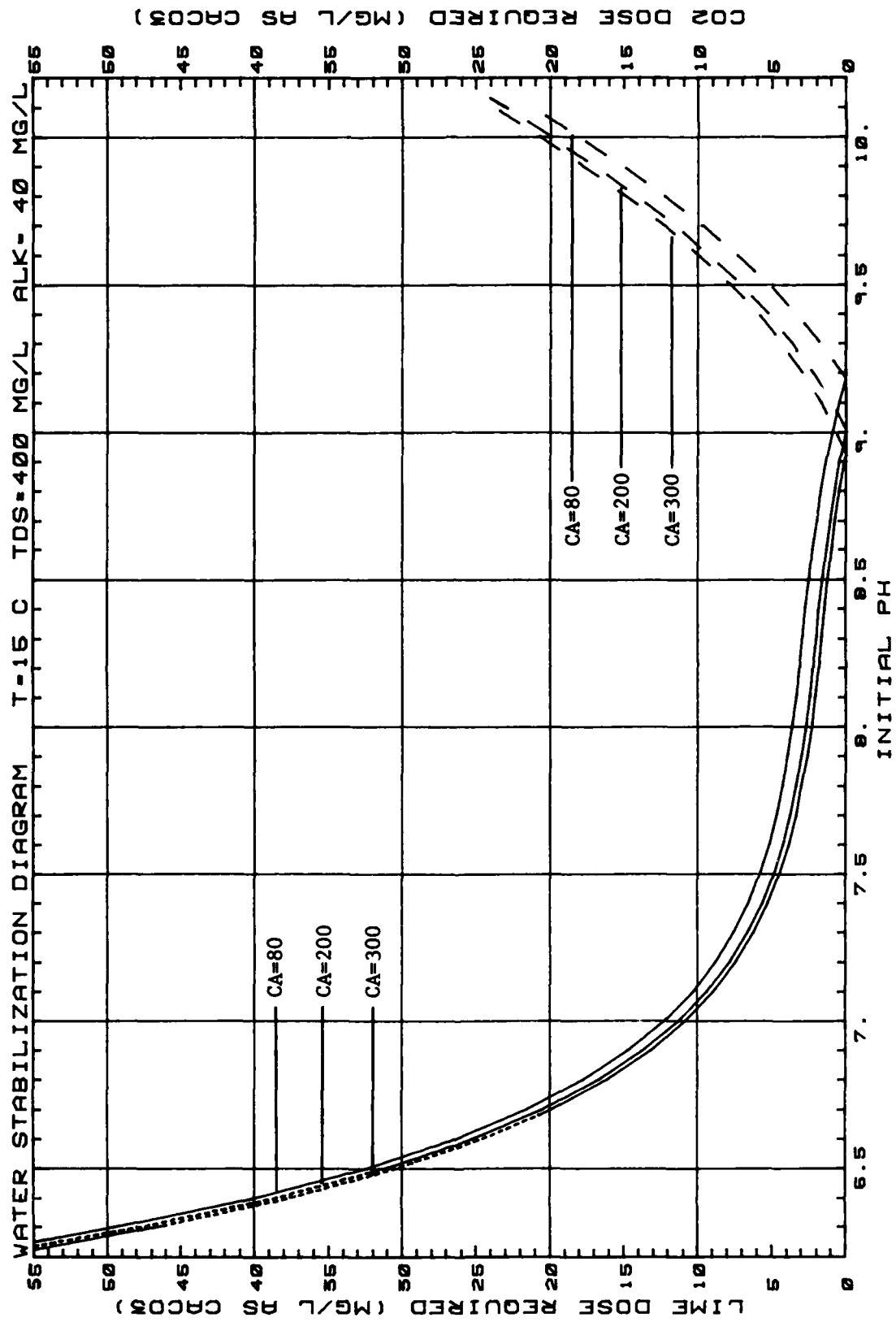


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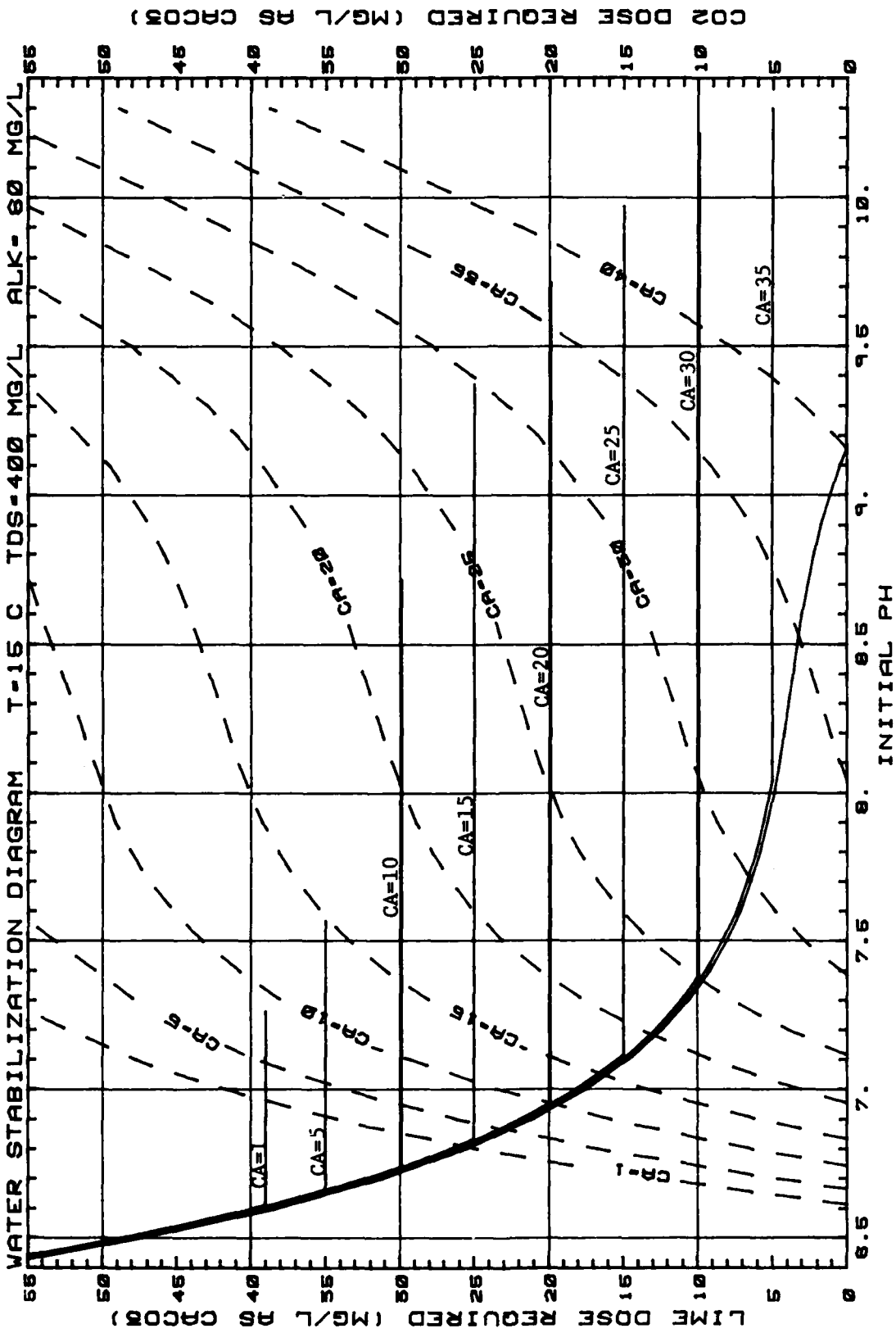


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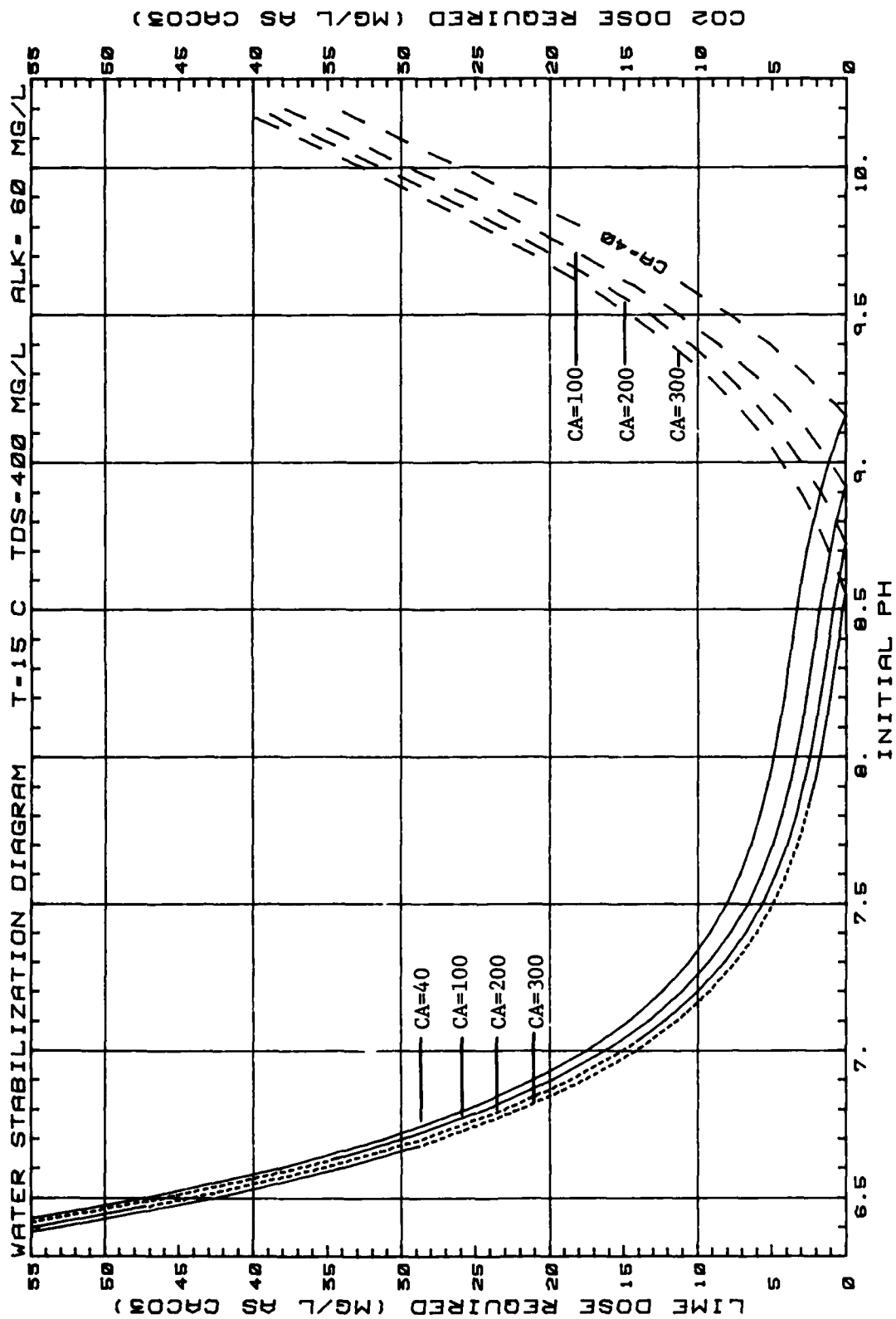


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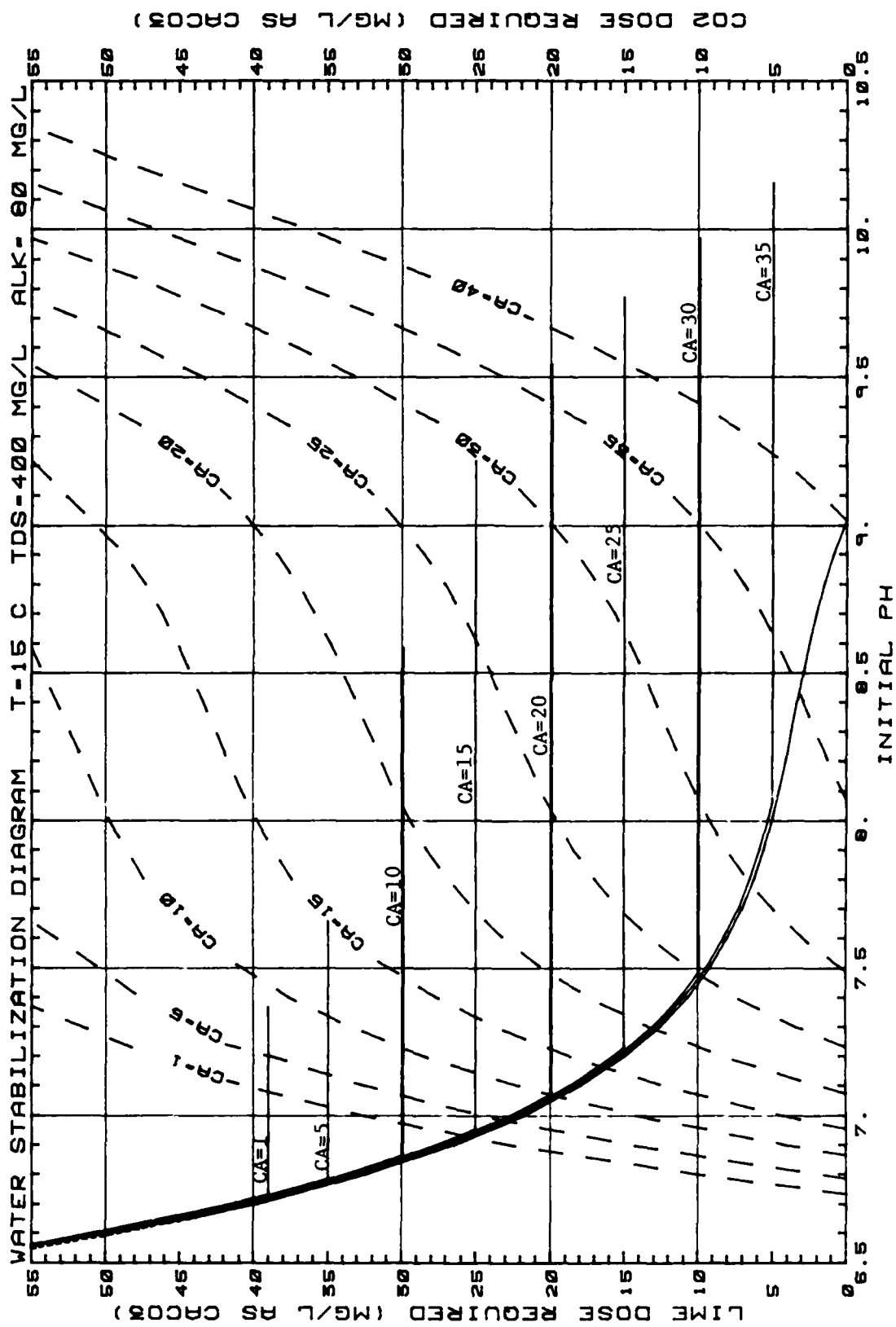


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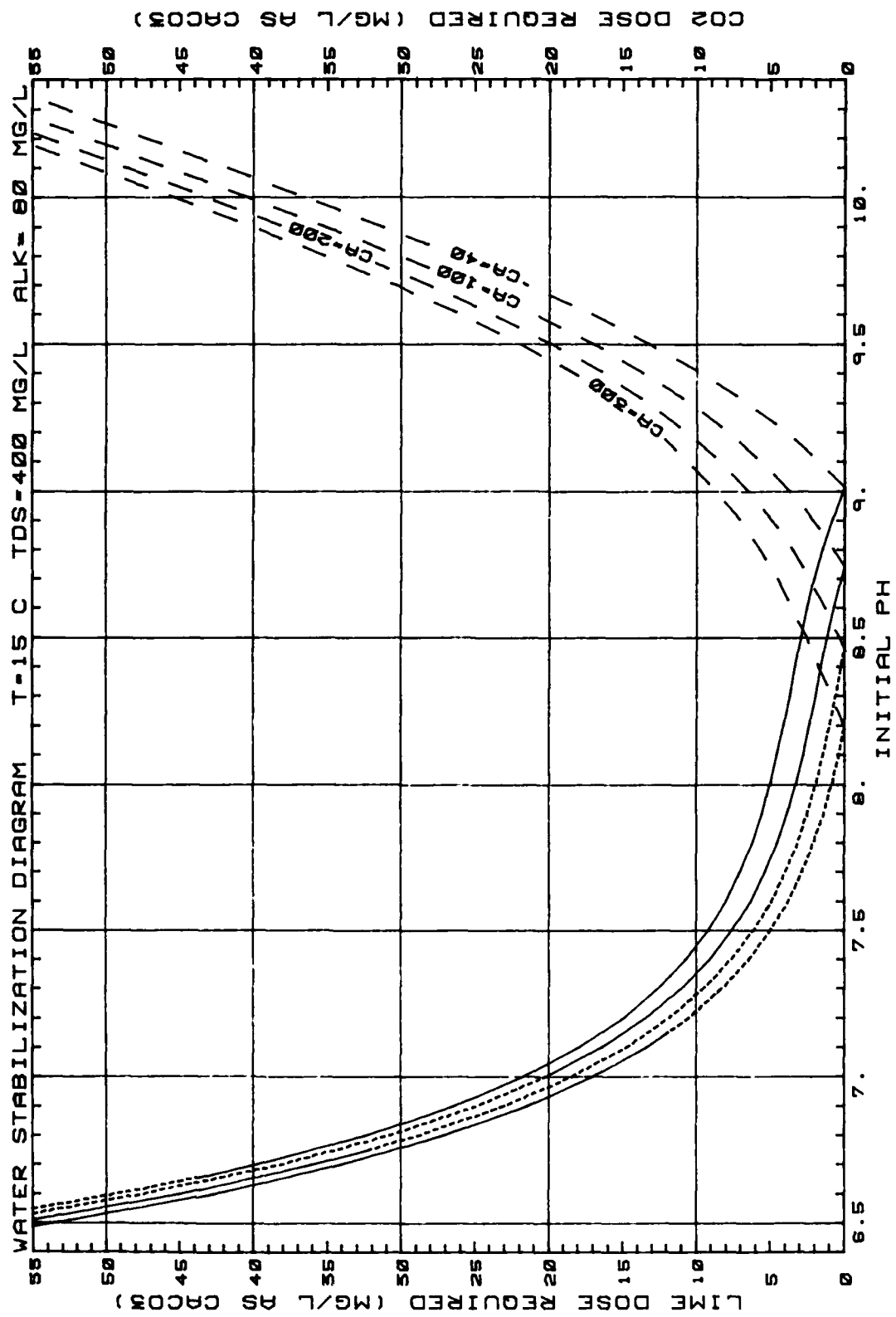


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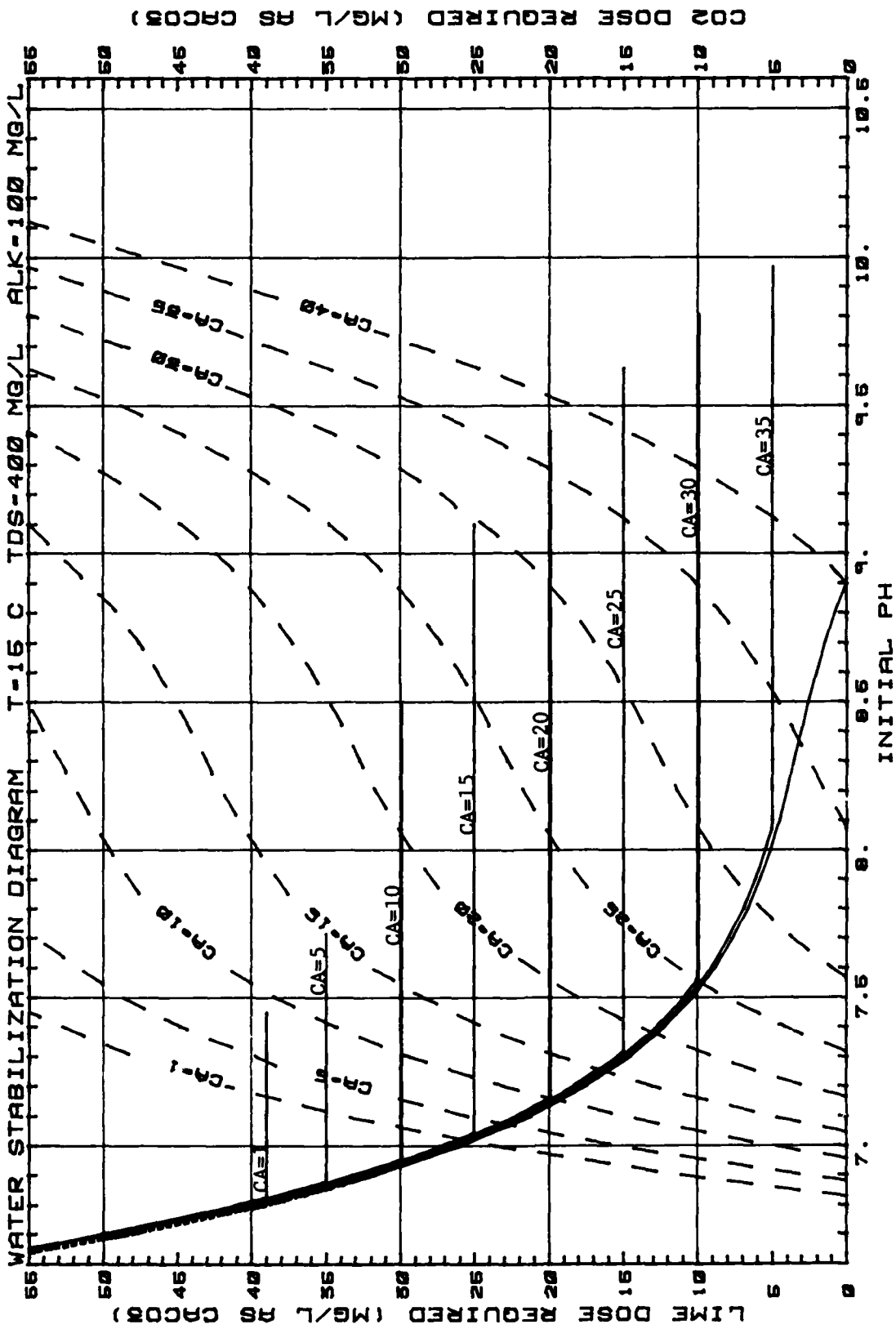


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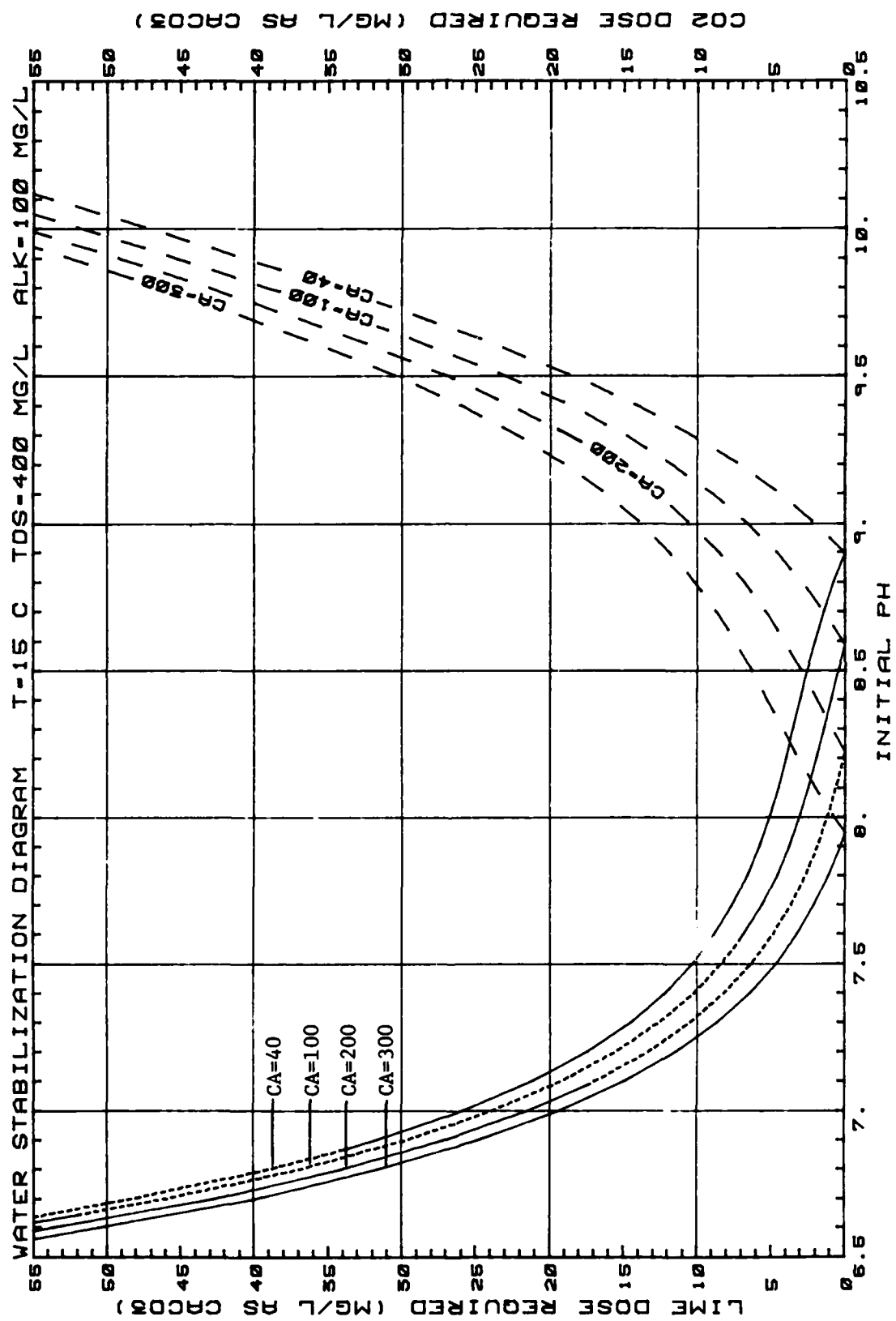


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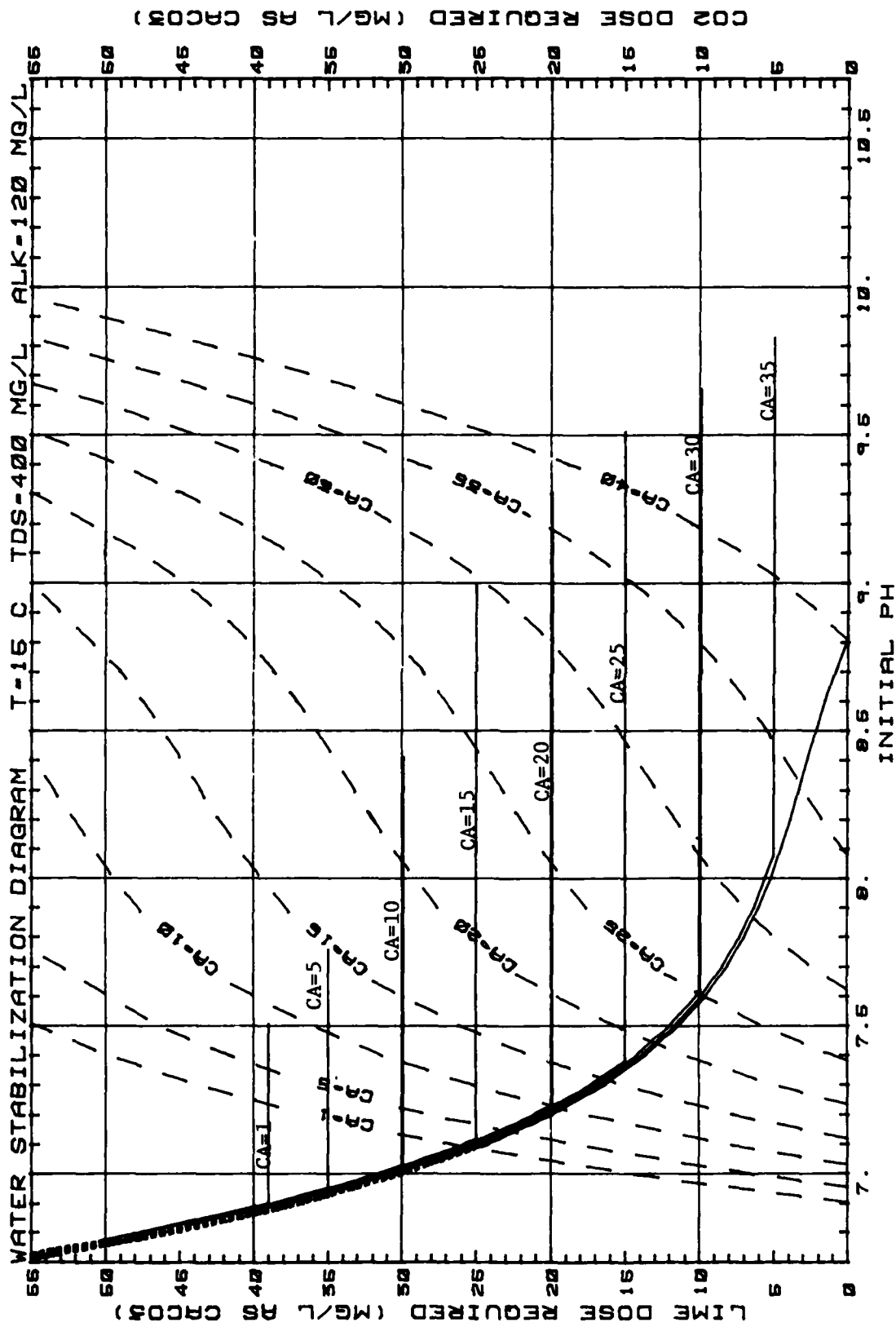


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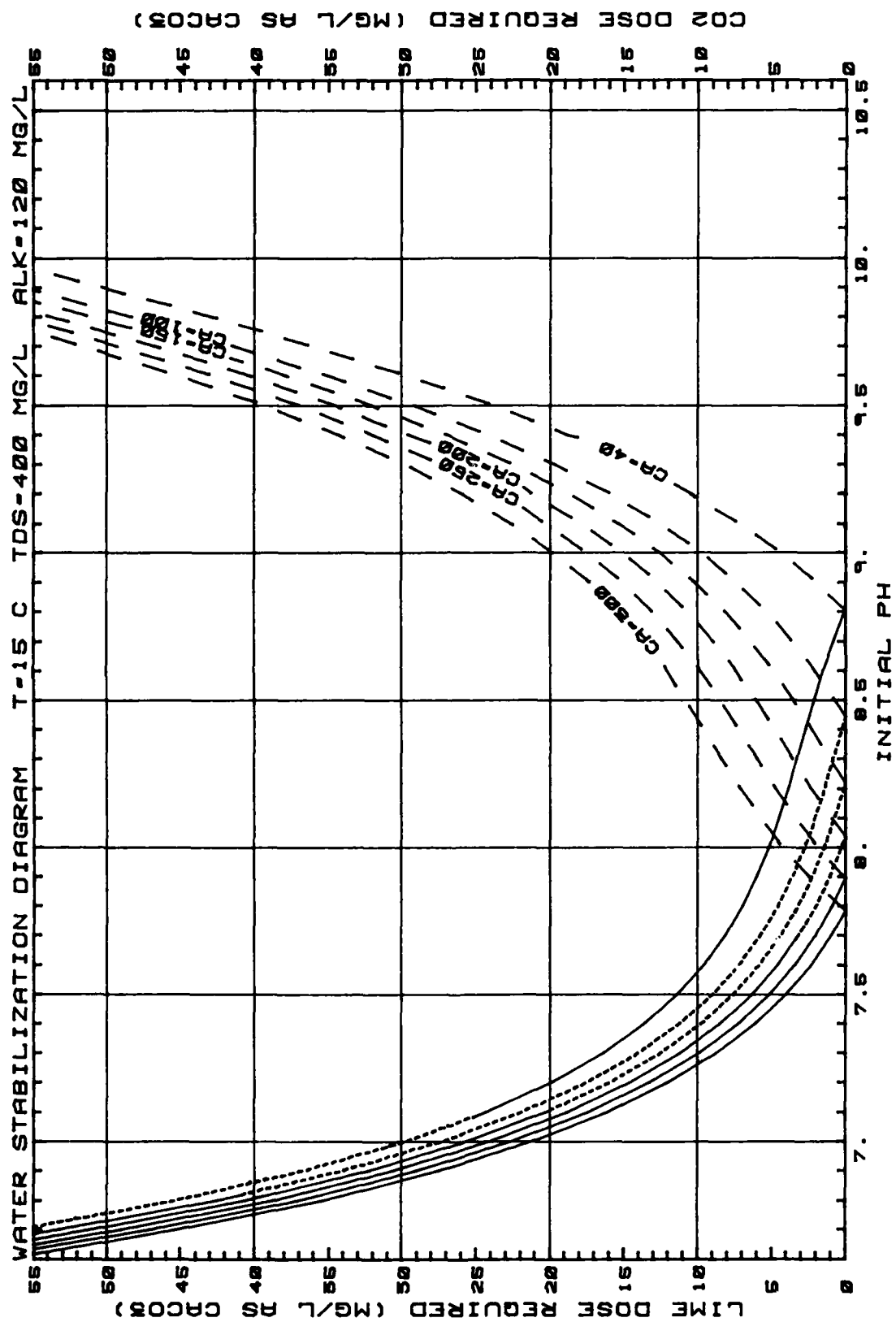


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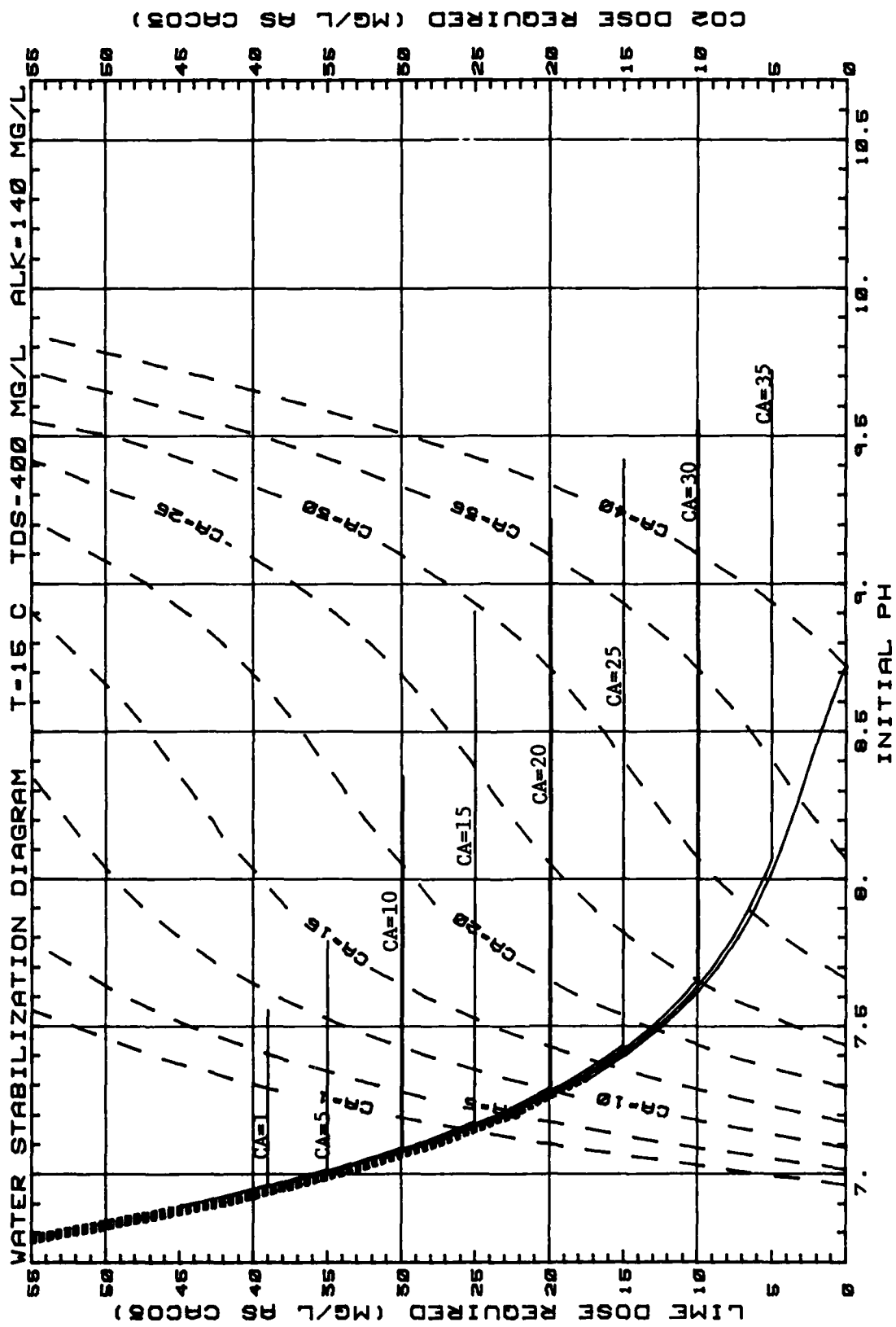


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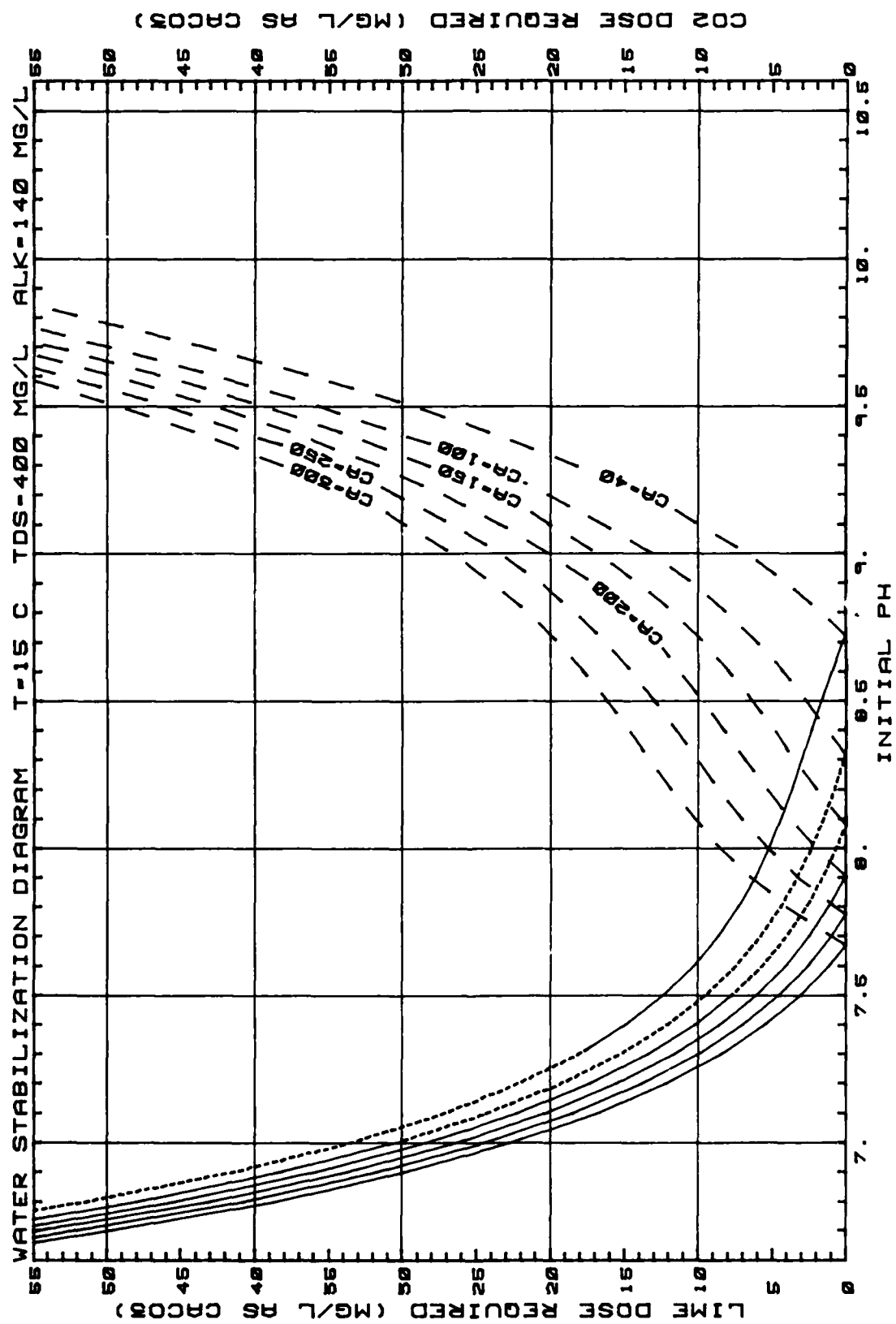


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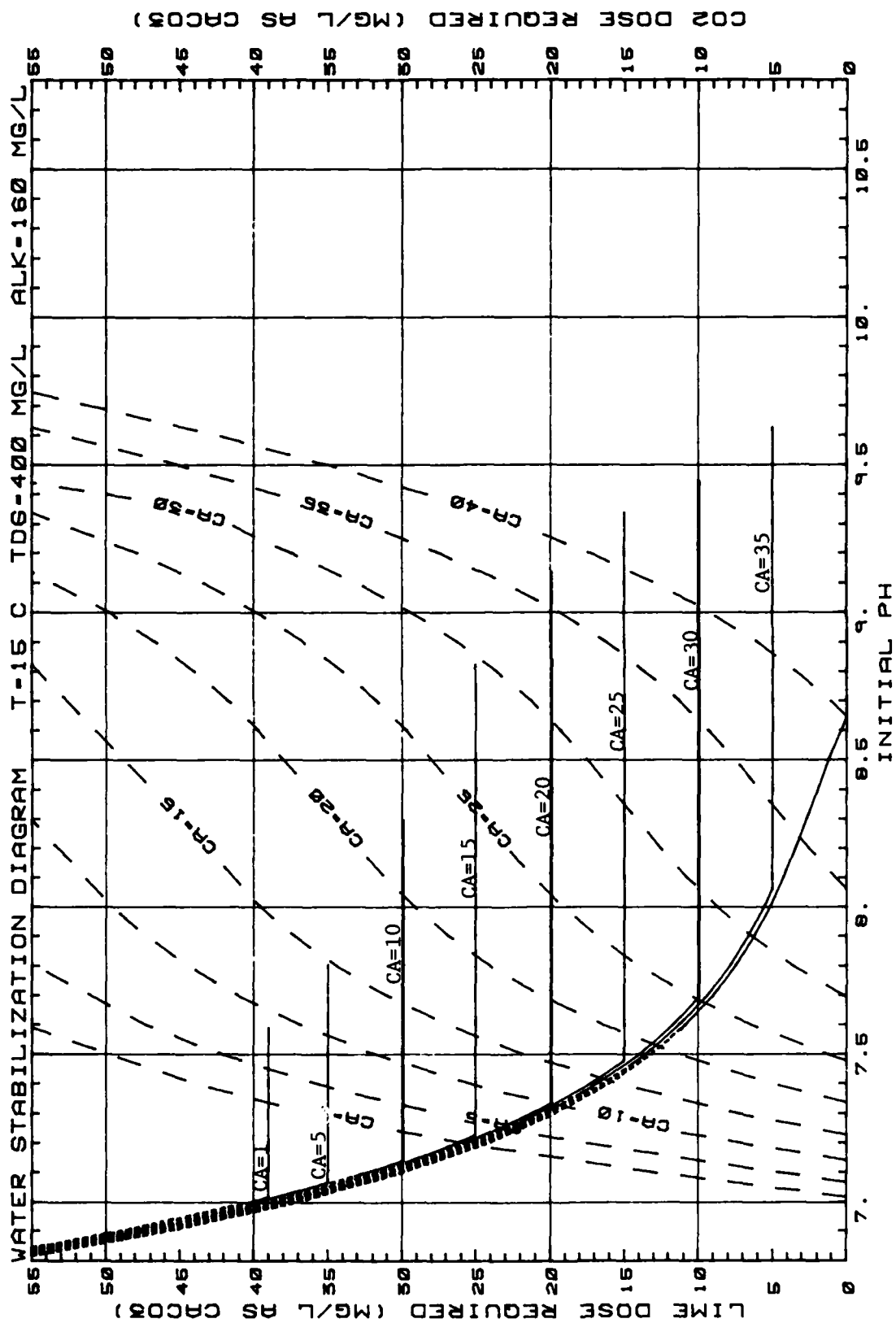


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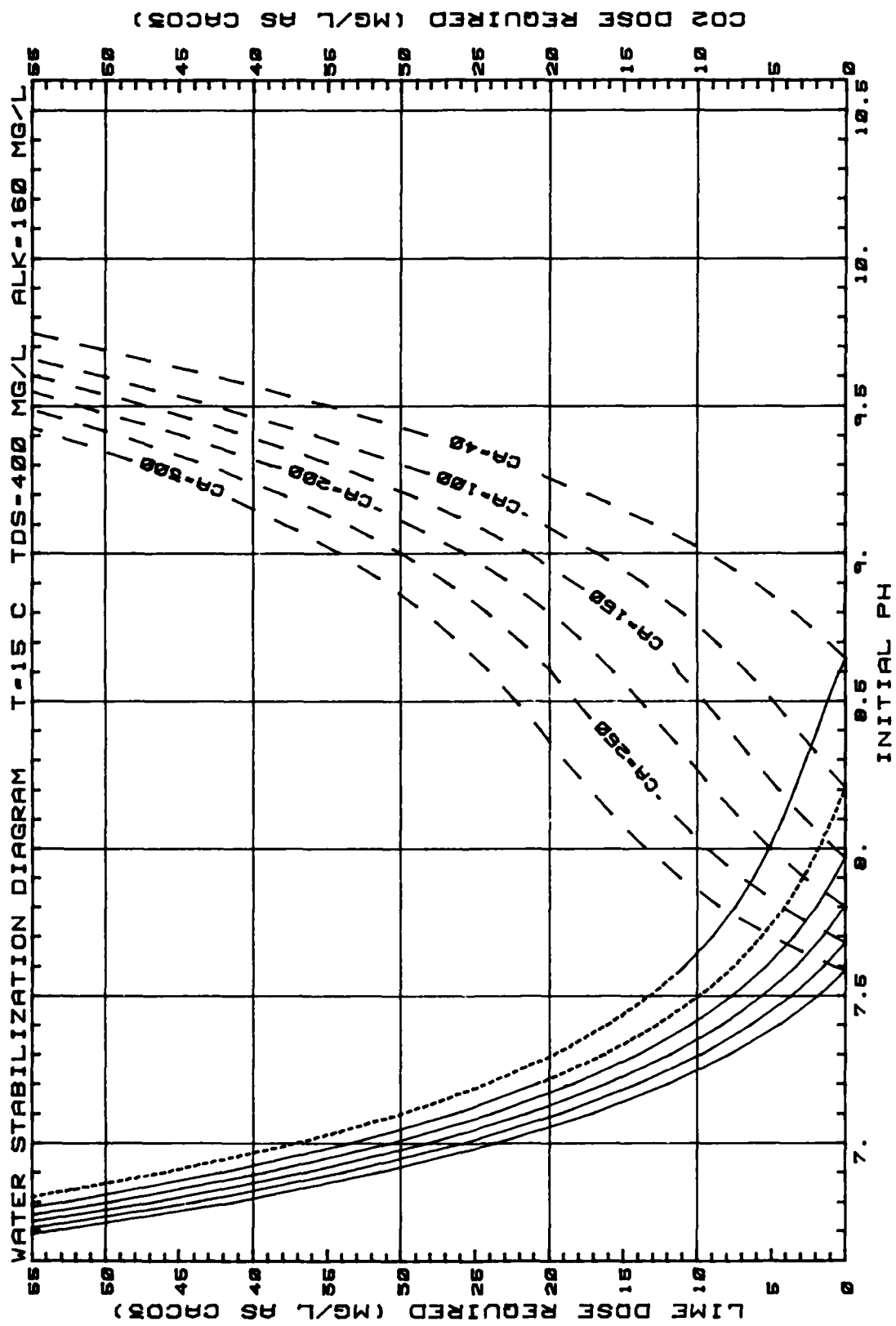


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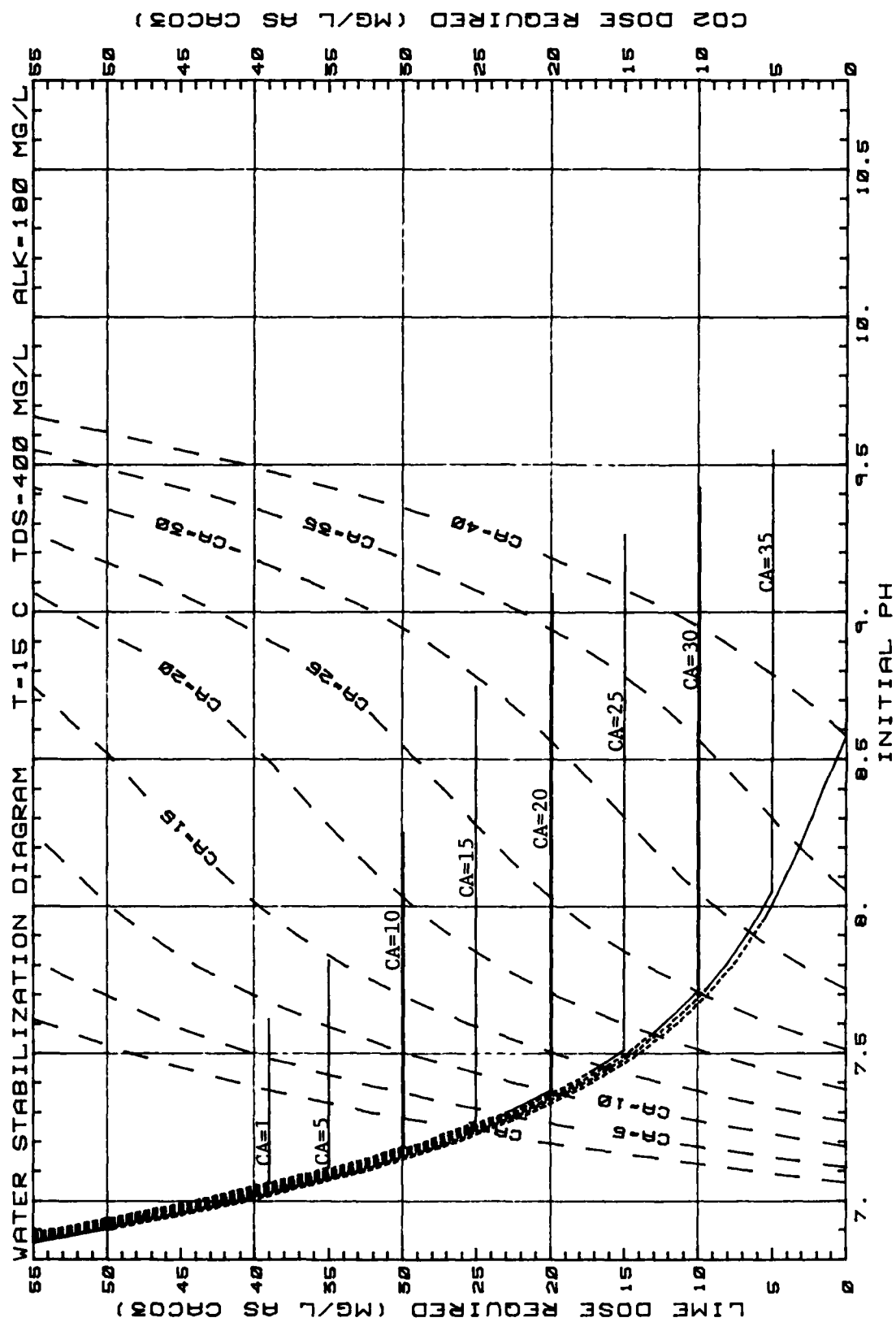


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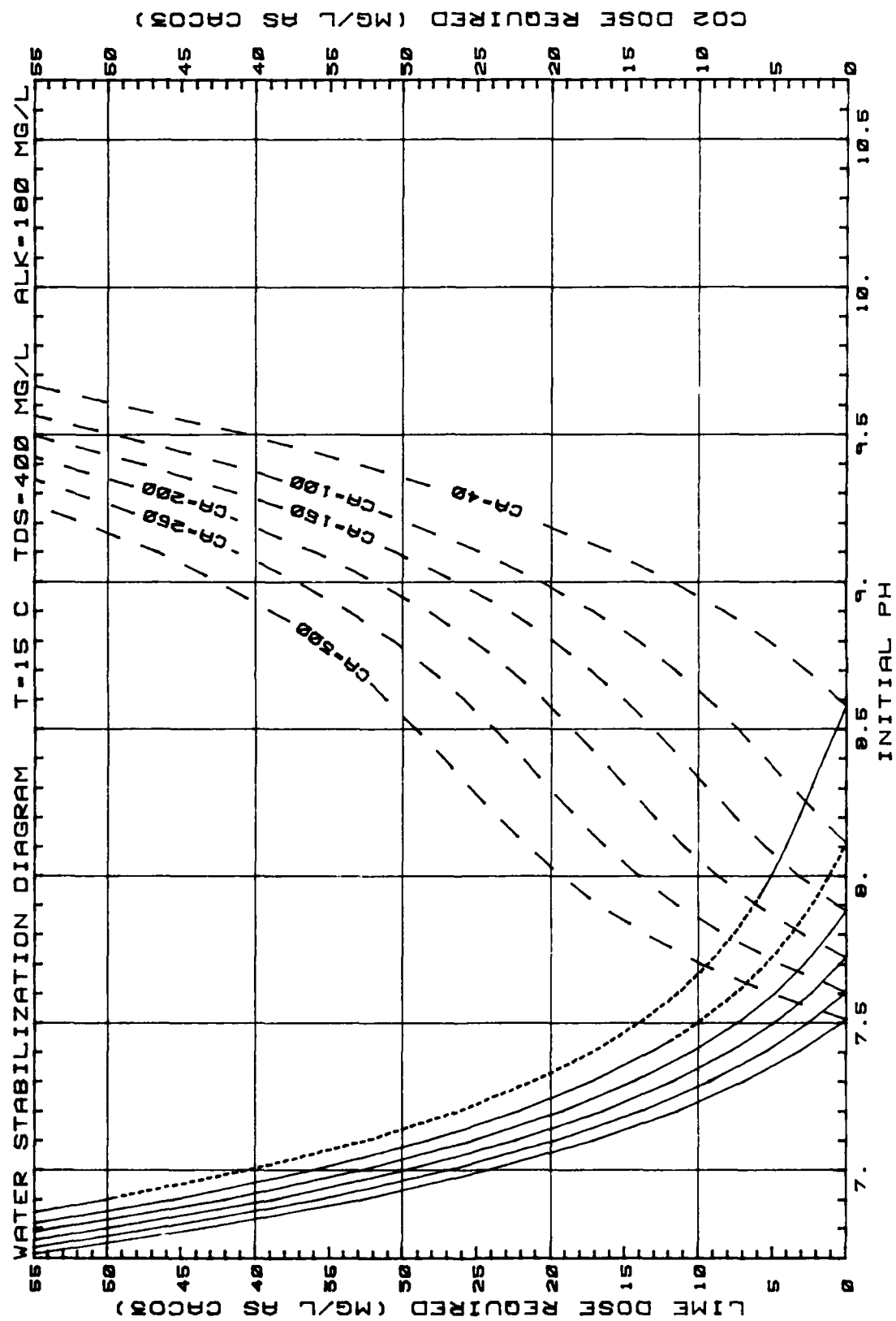


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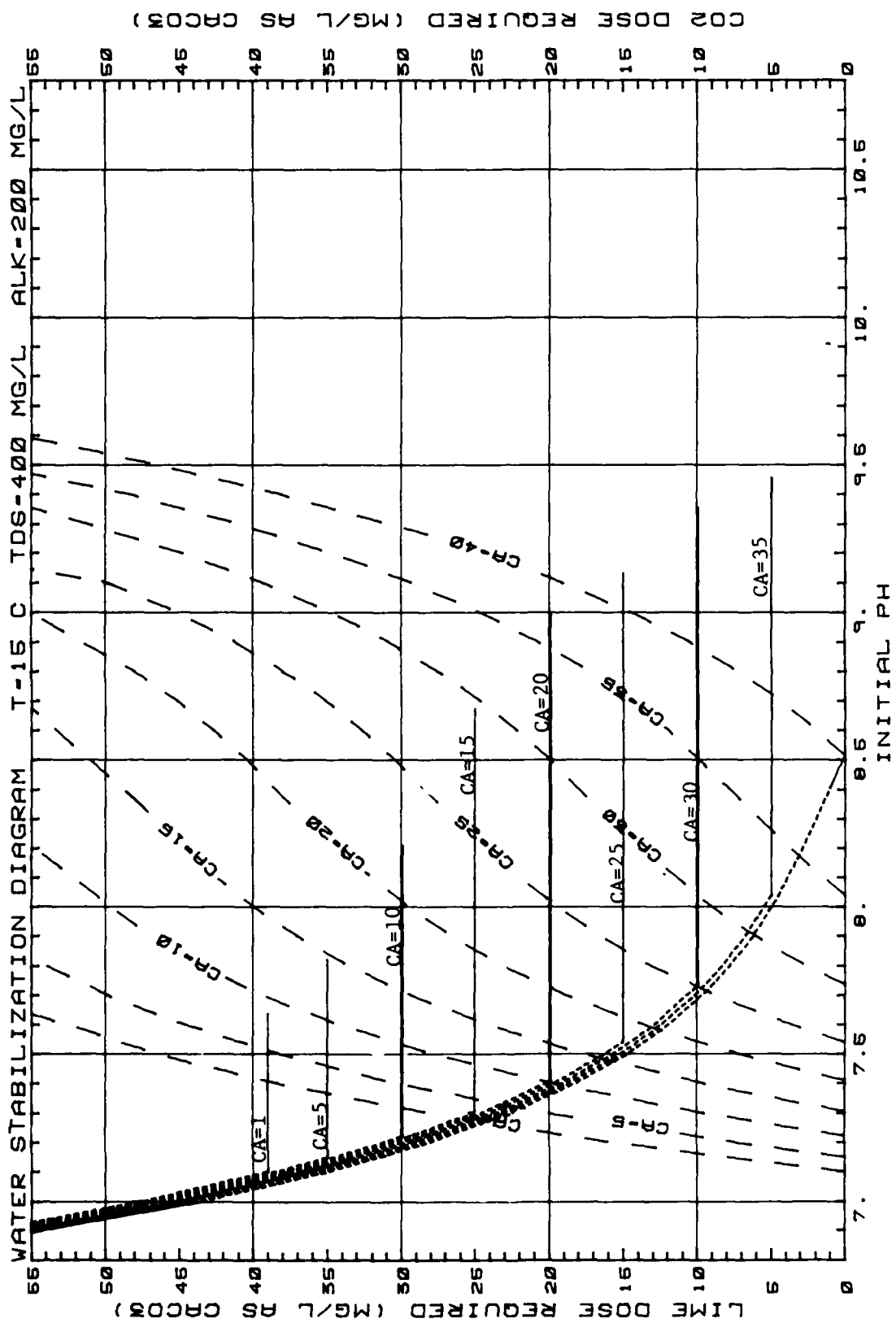


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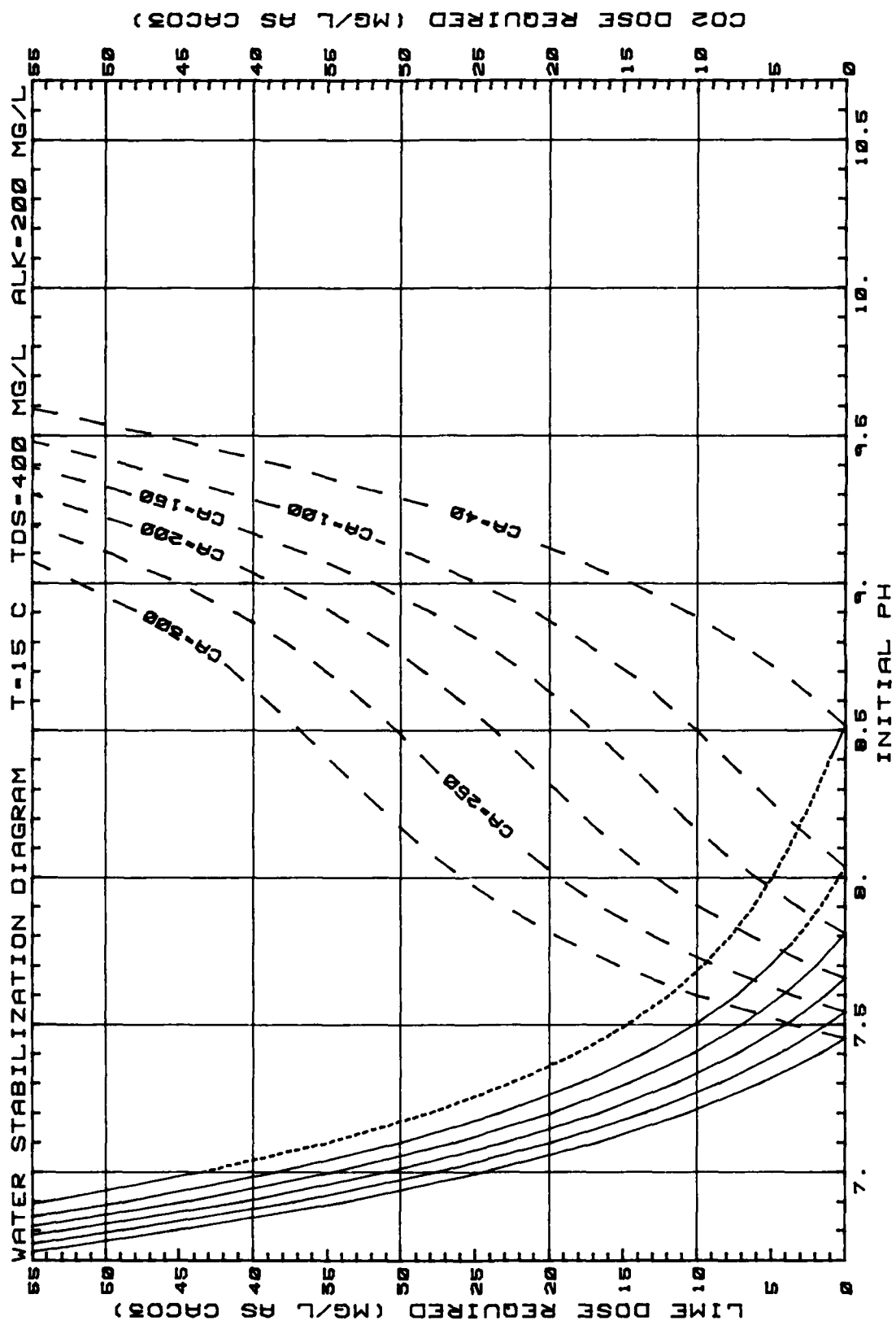


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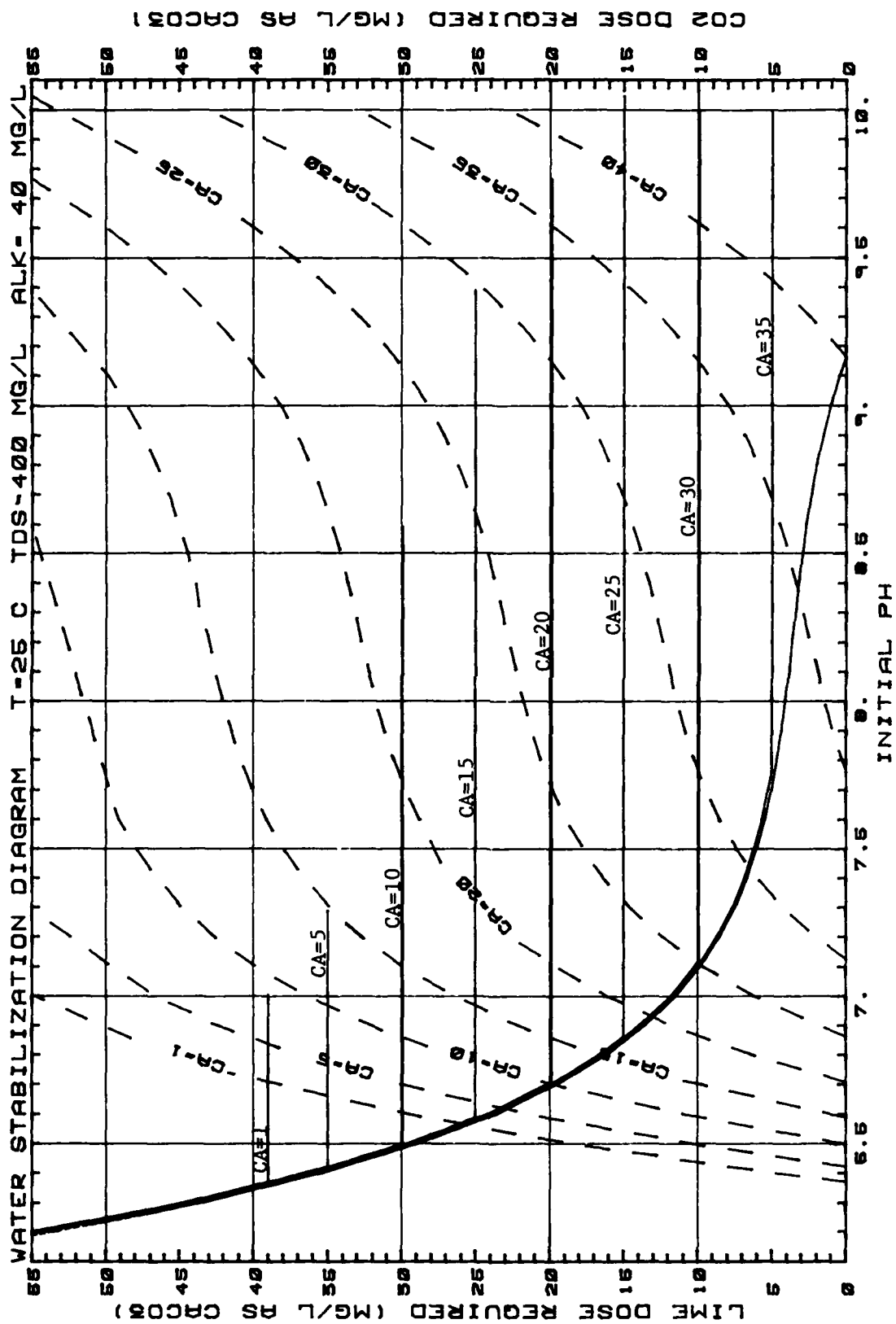


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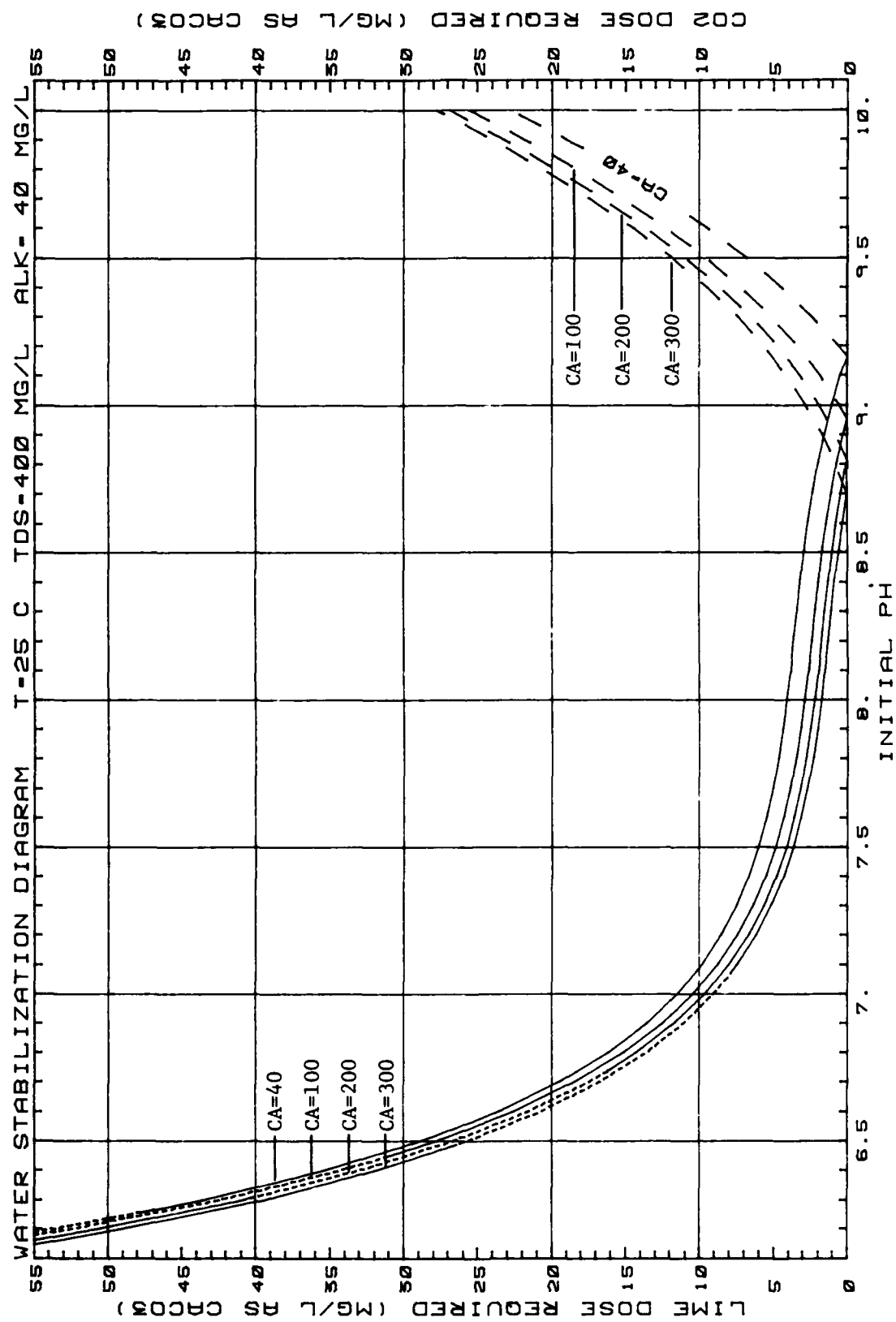


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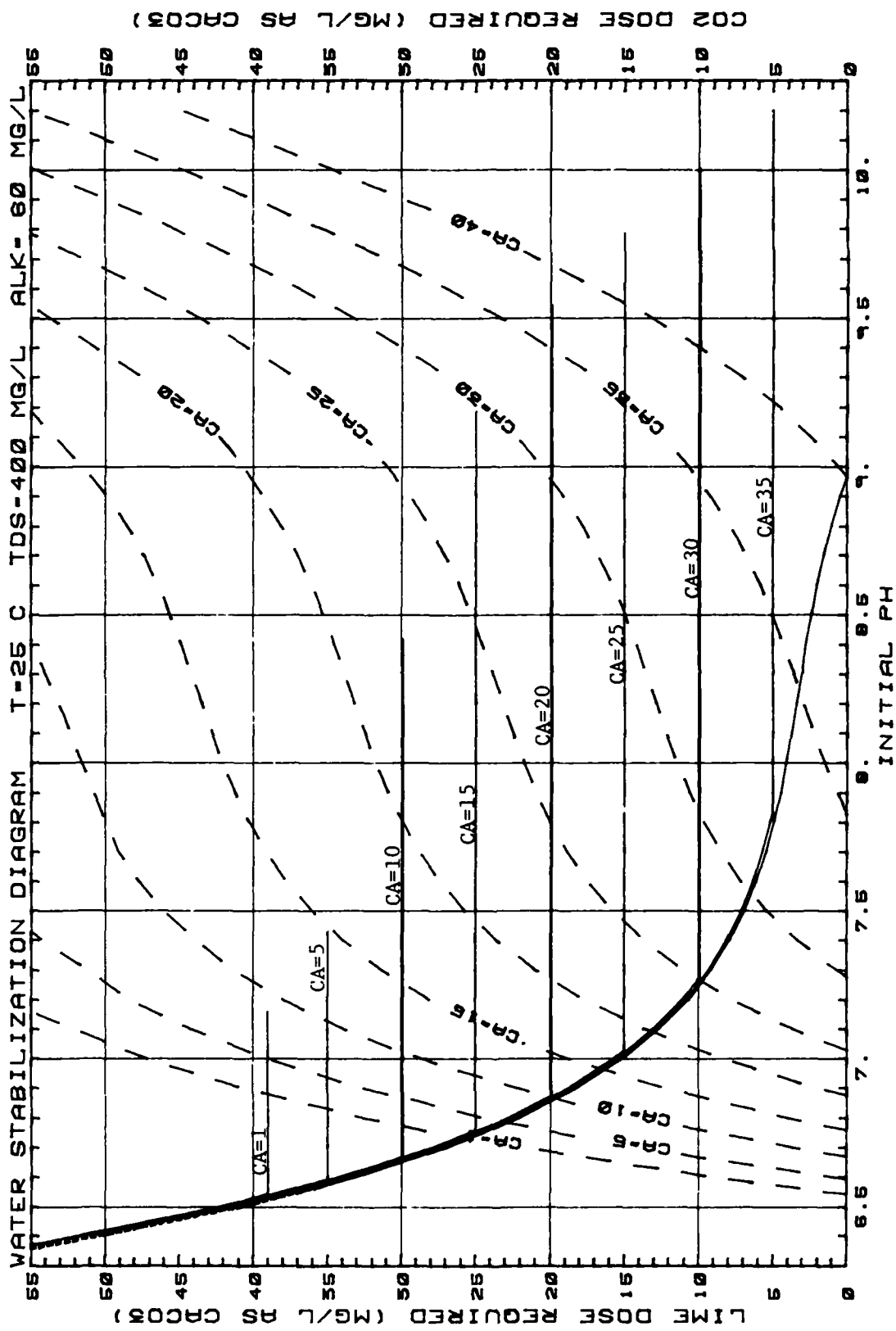


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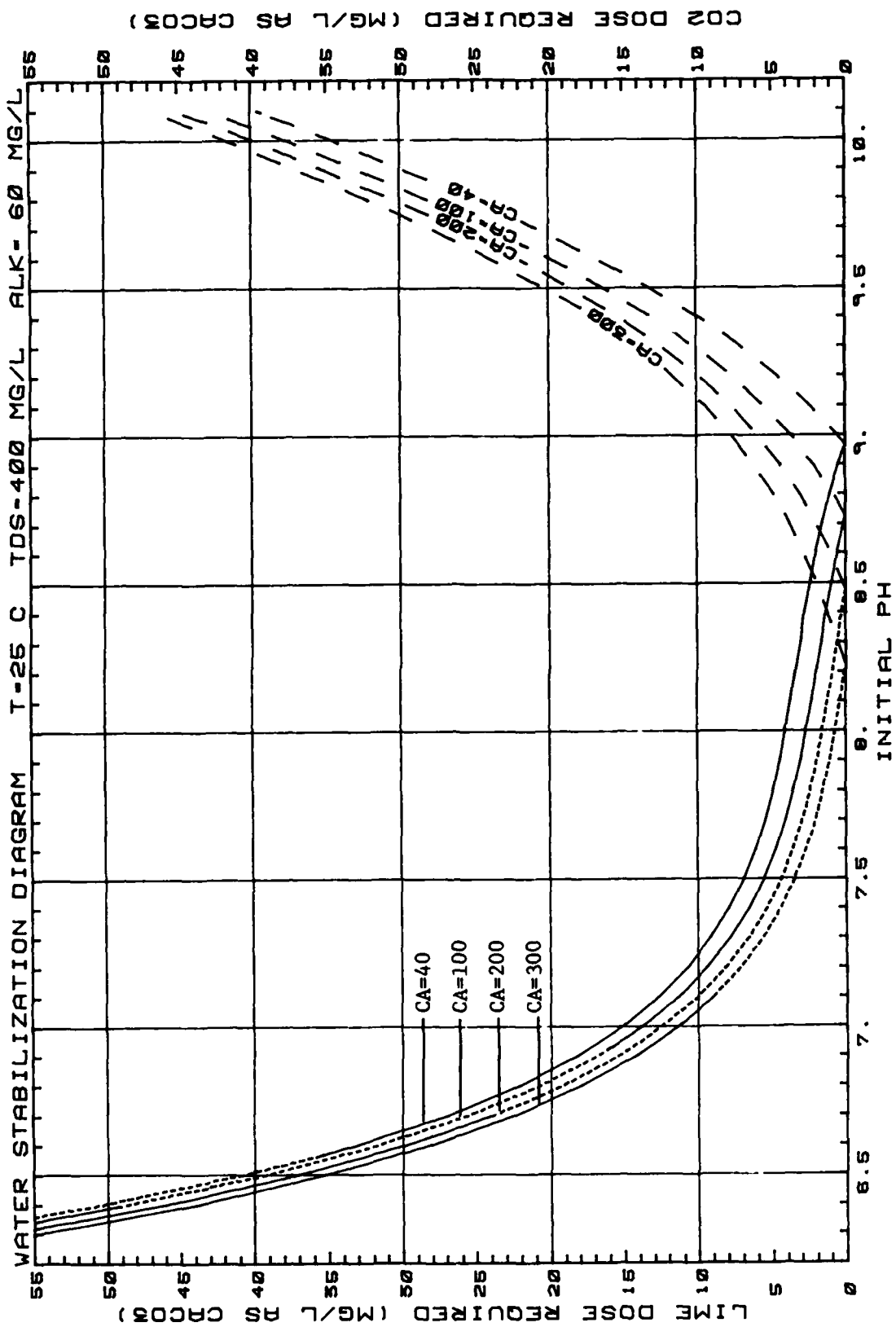


DIAGRAM A66

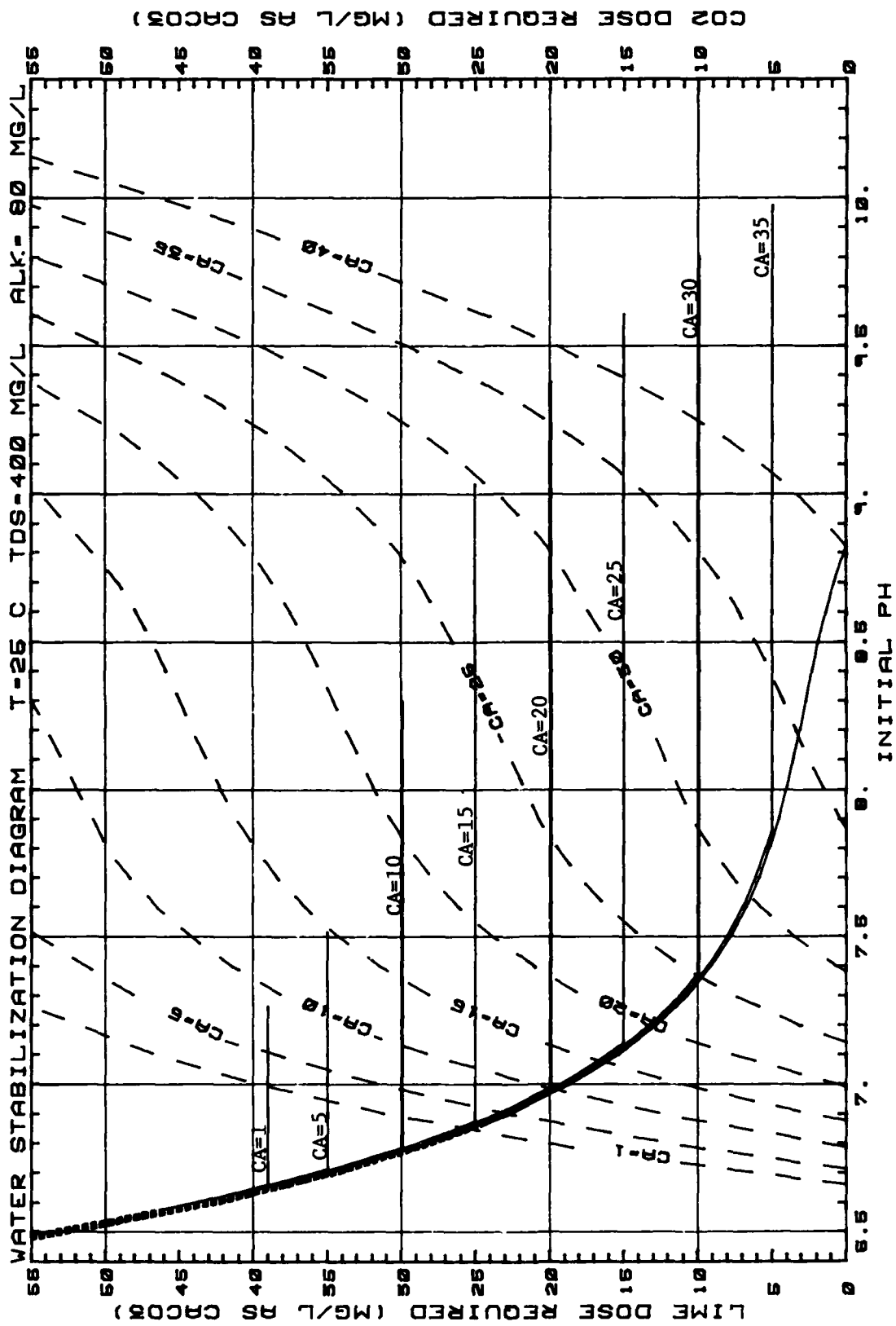


DIAGRAM A67

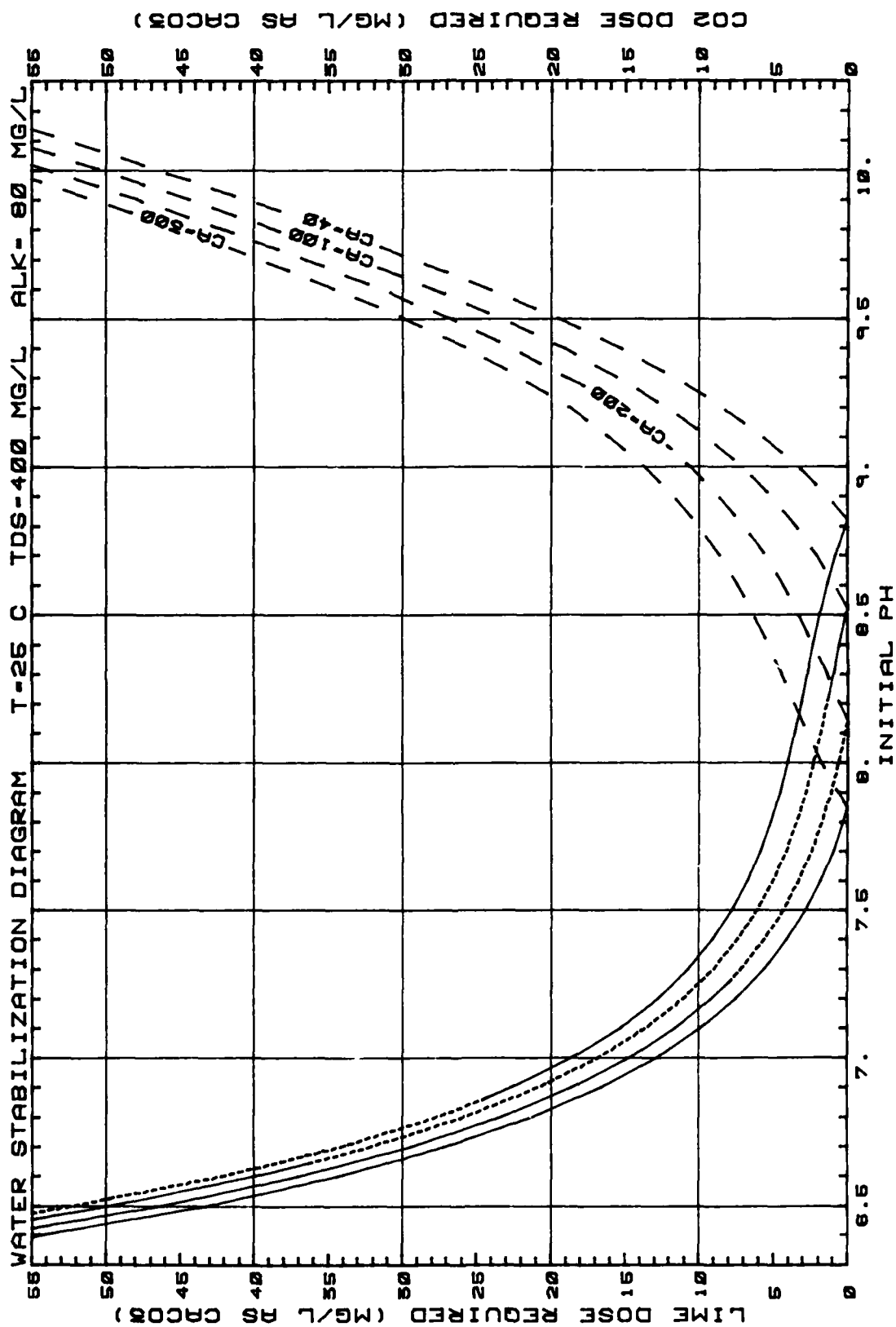


DIAGRAM A68

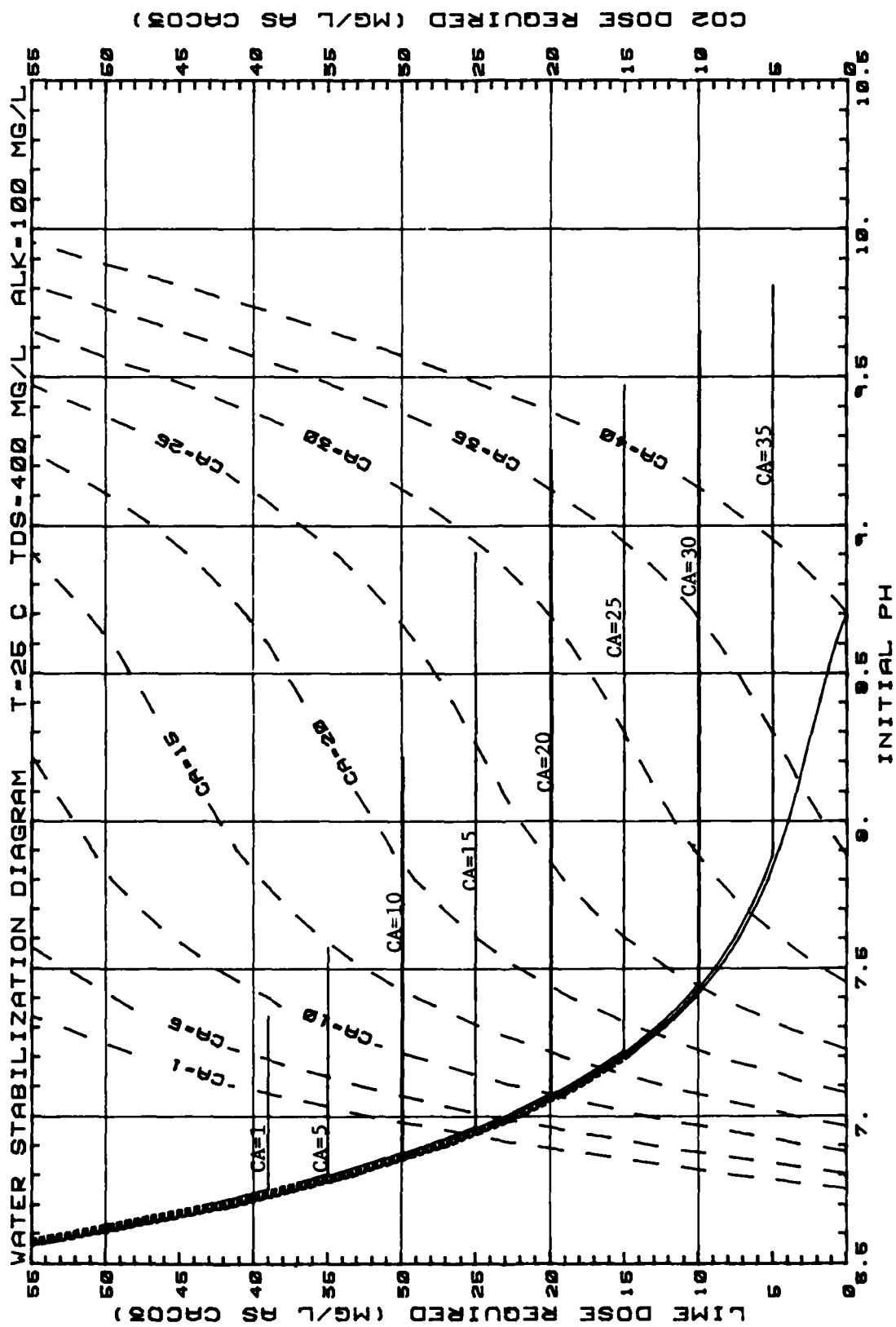


DIAGRAM A69

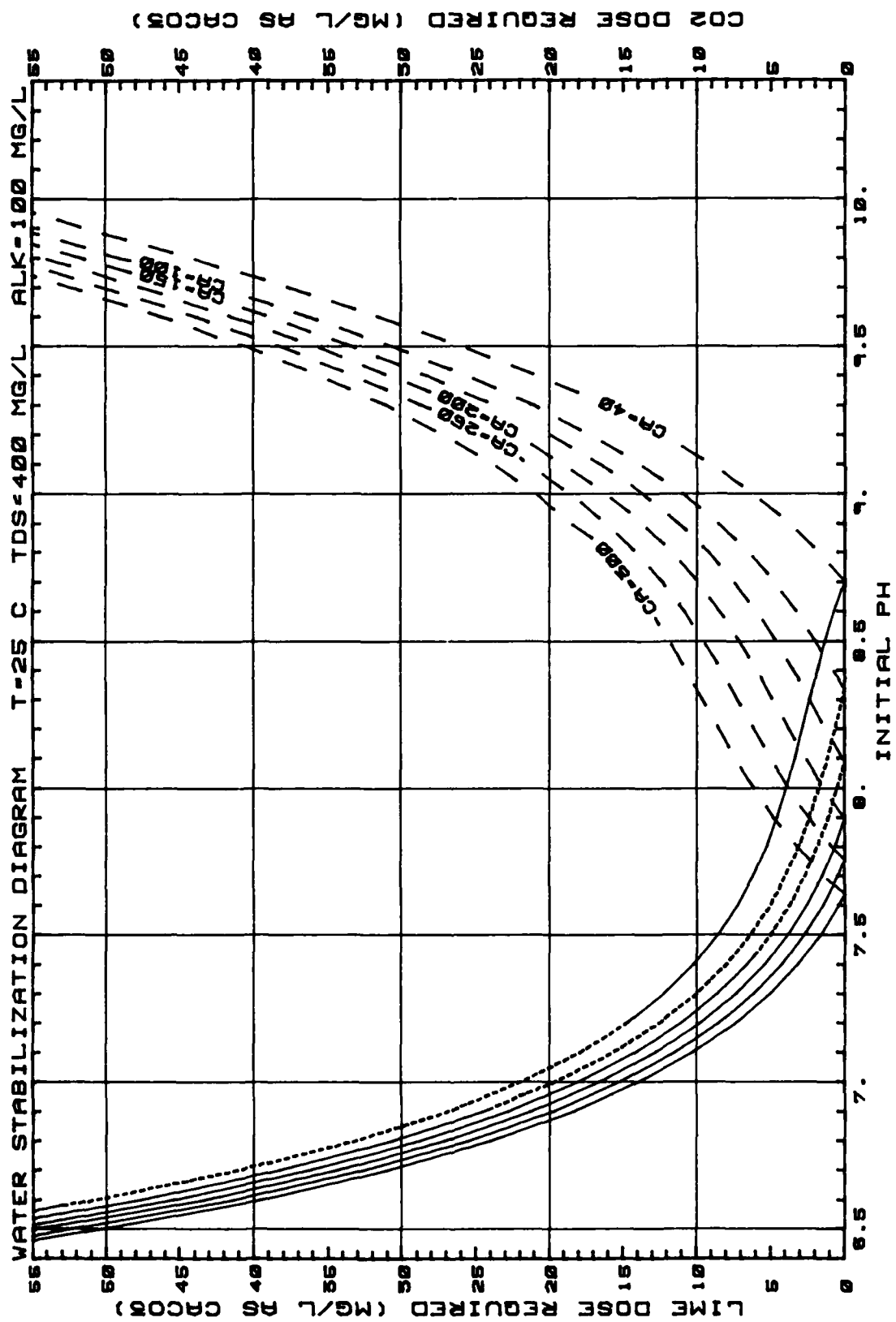


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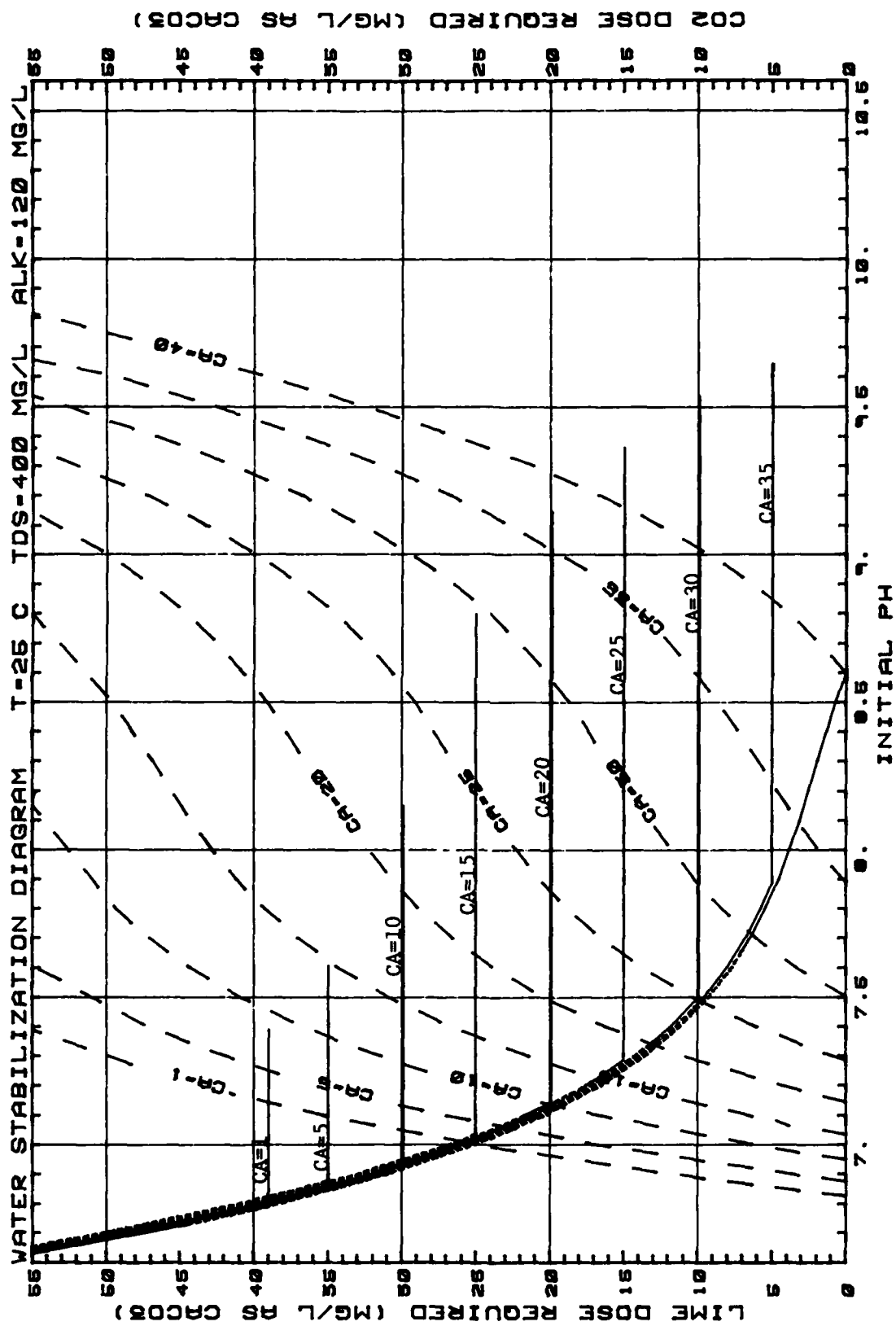


DIAGRAM A71

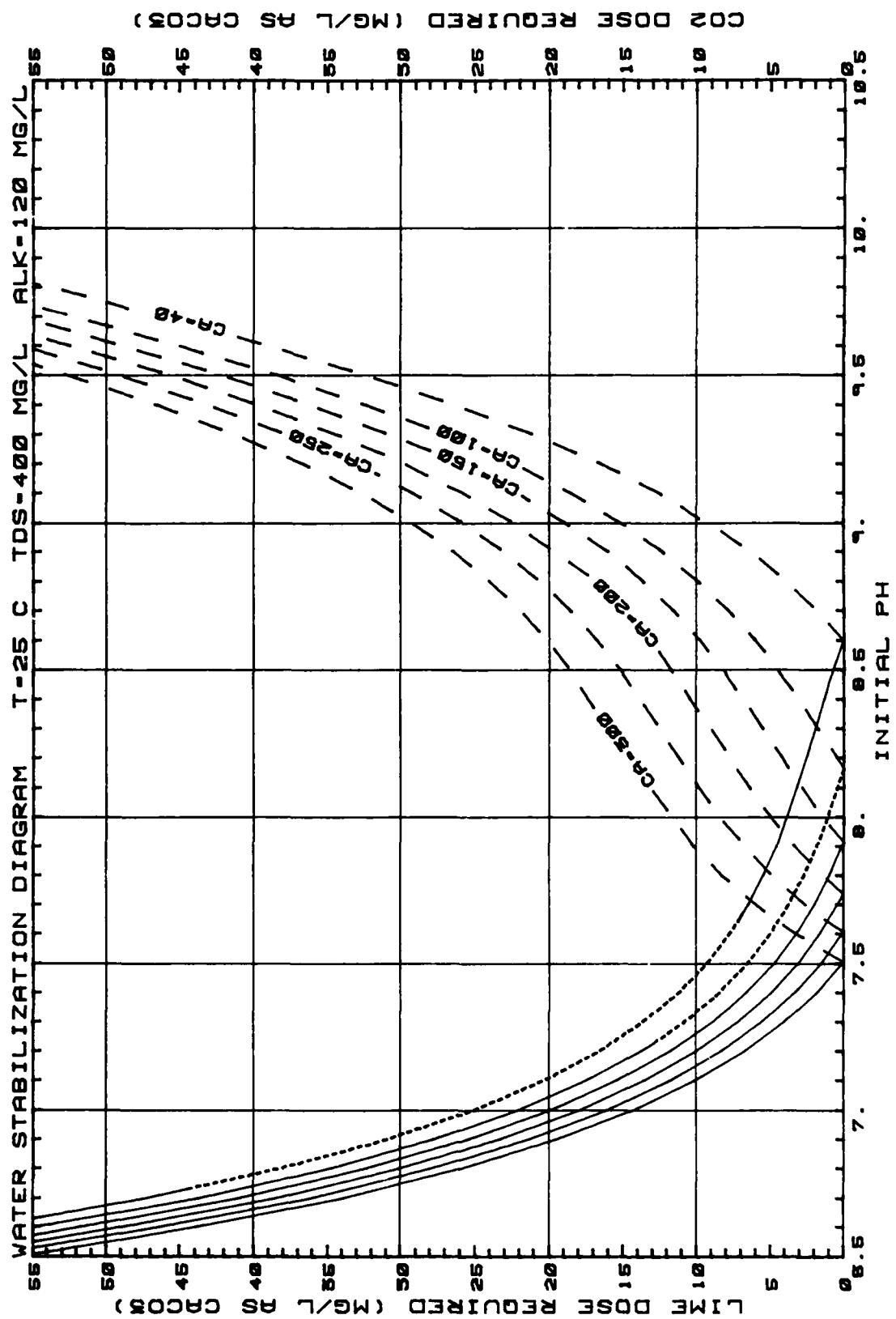


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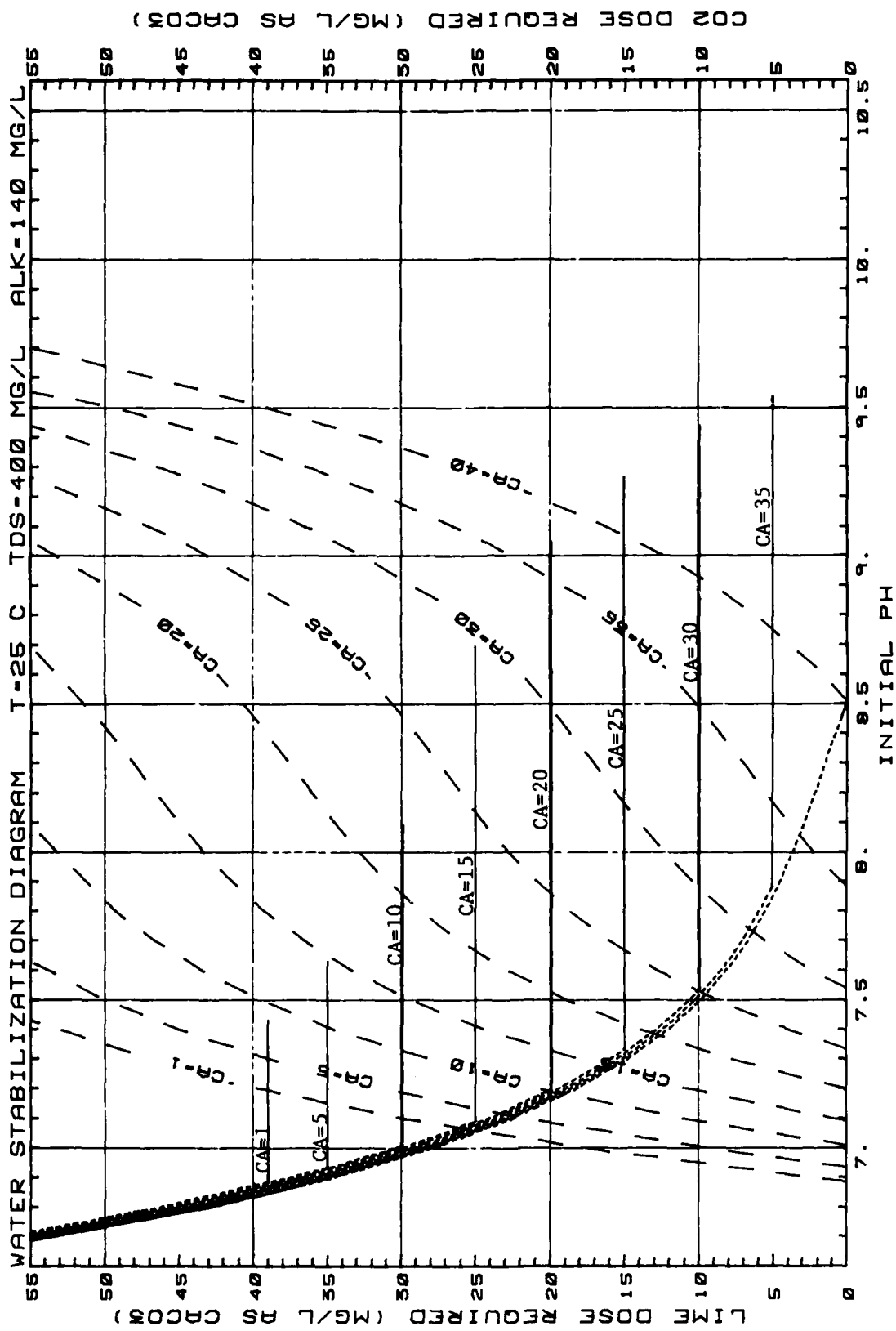


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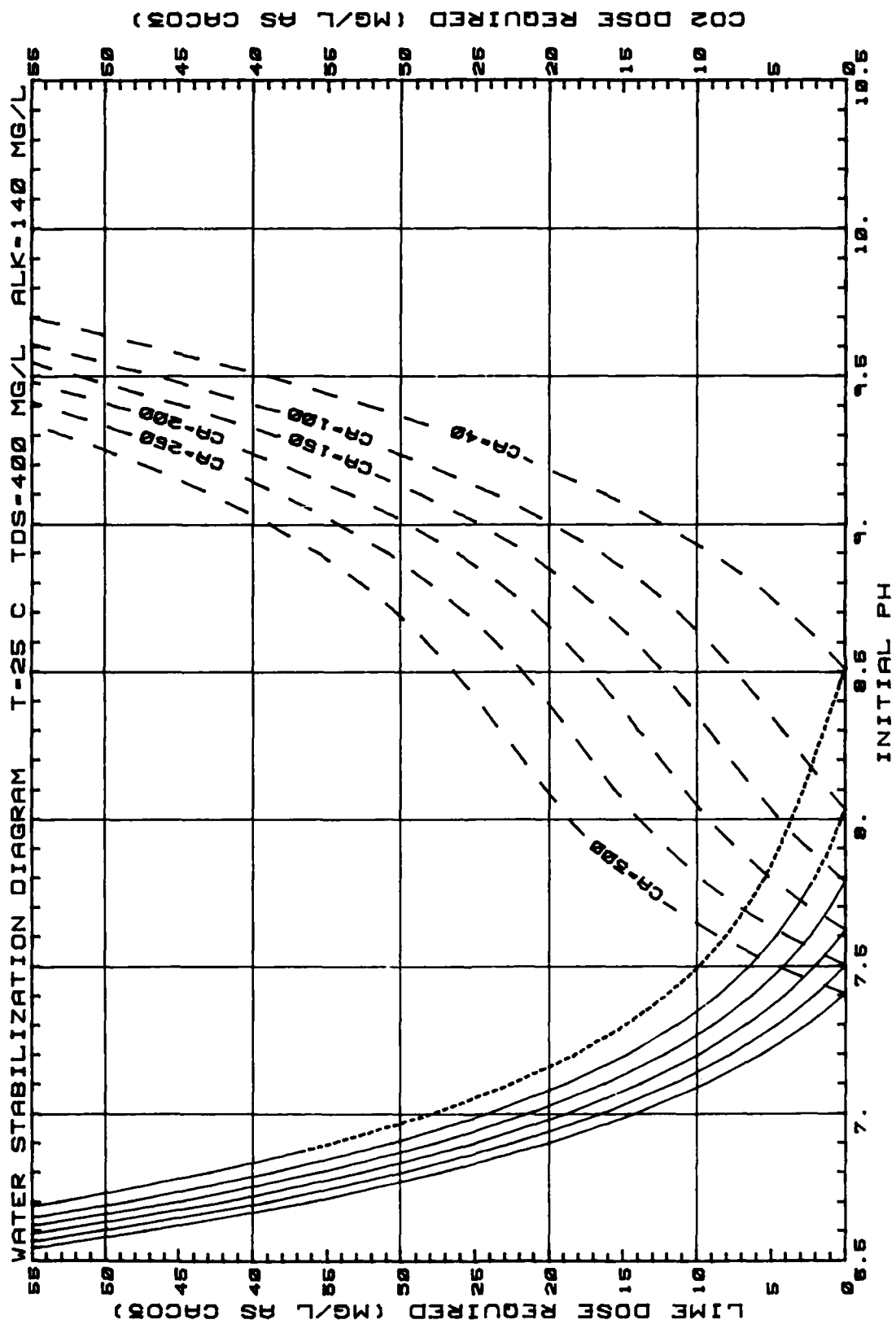


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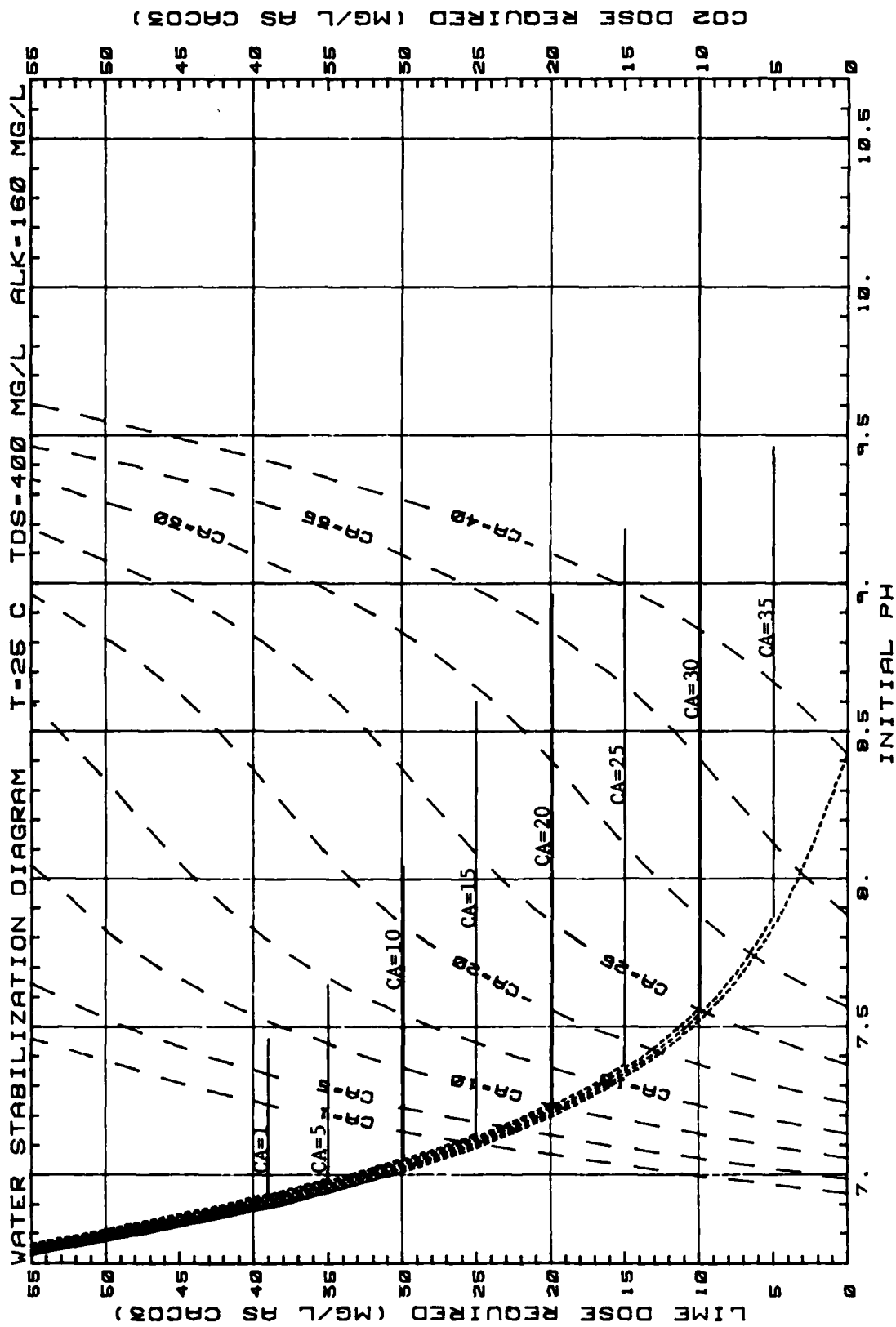


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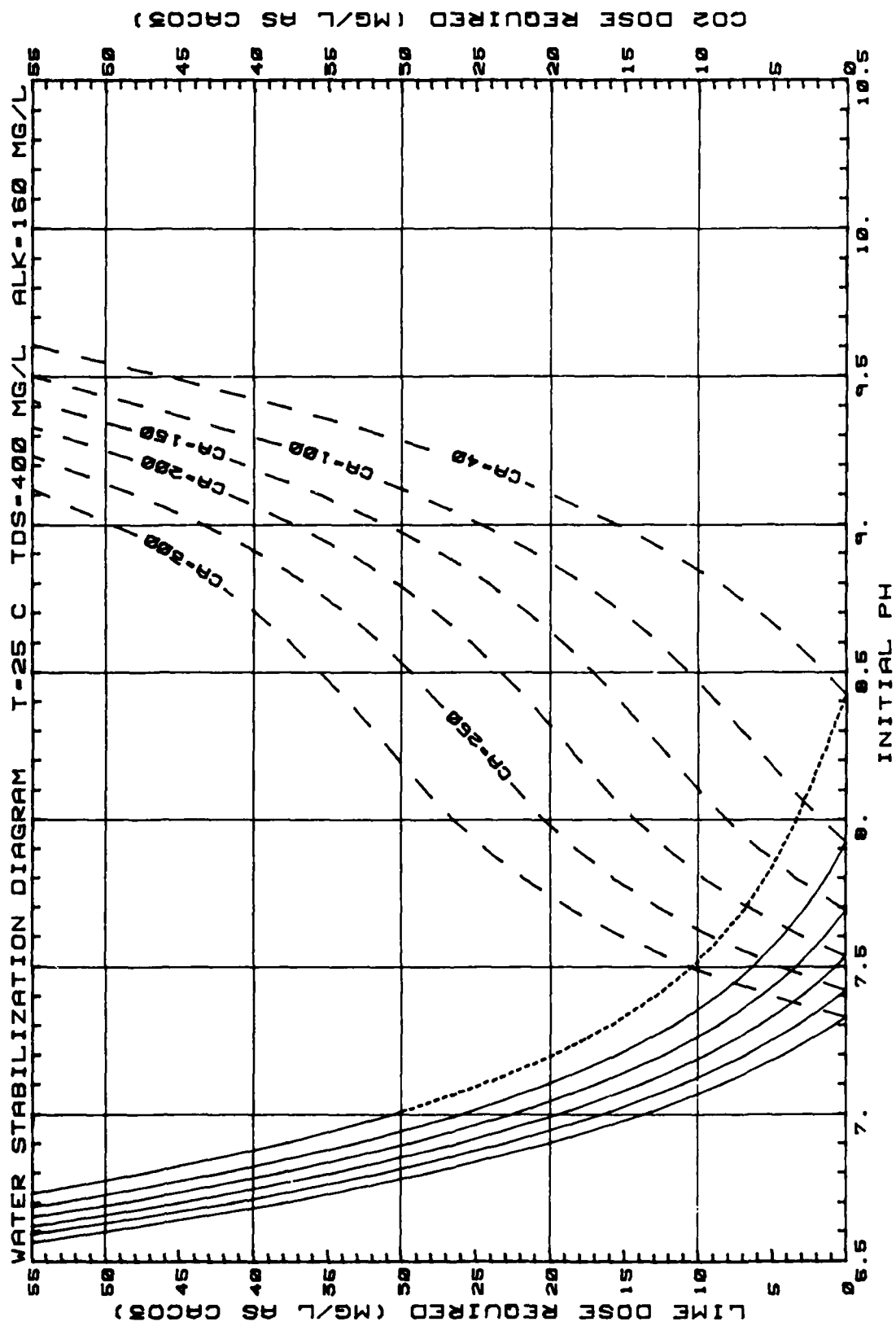


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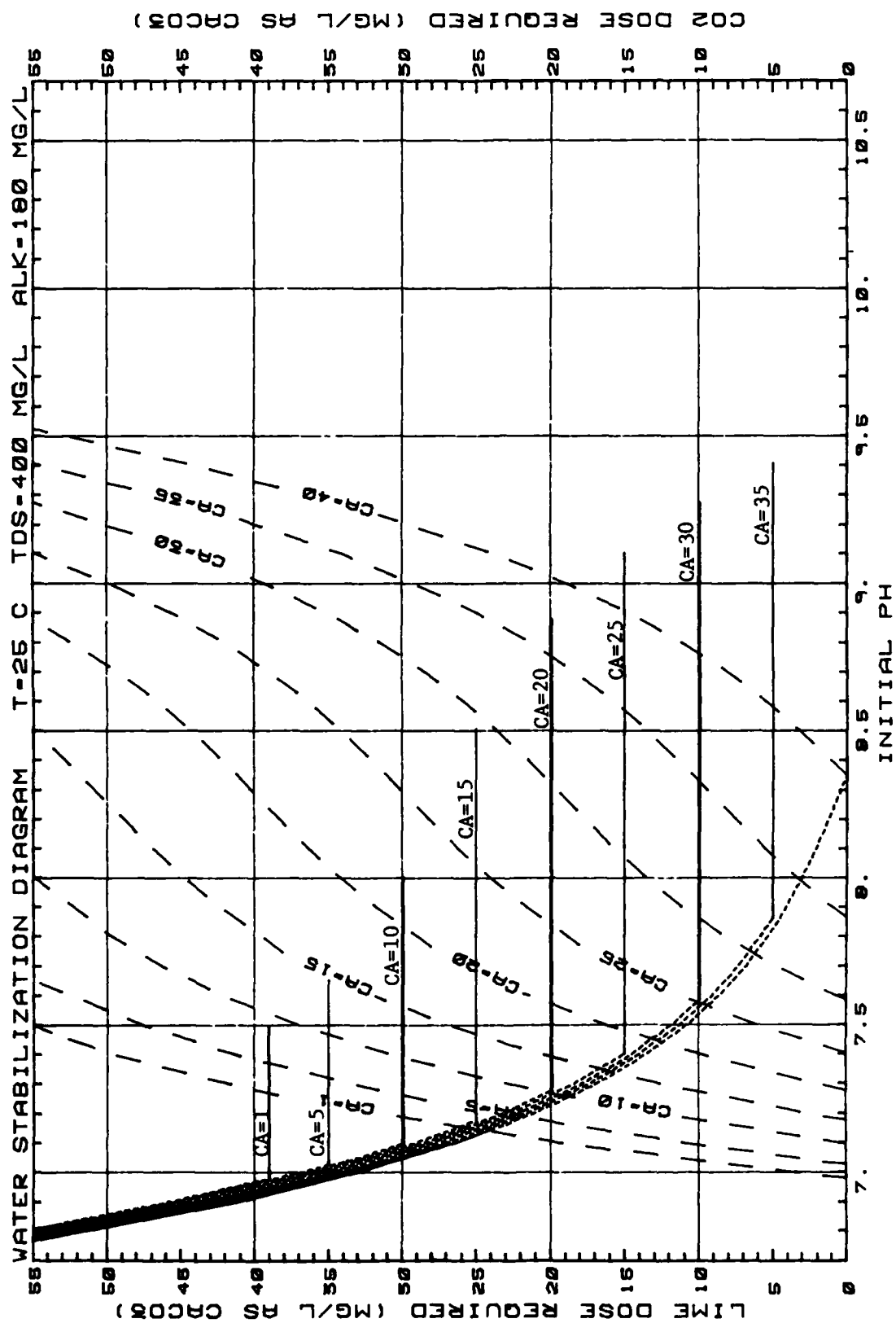


DIAGRAM A77

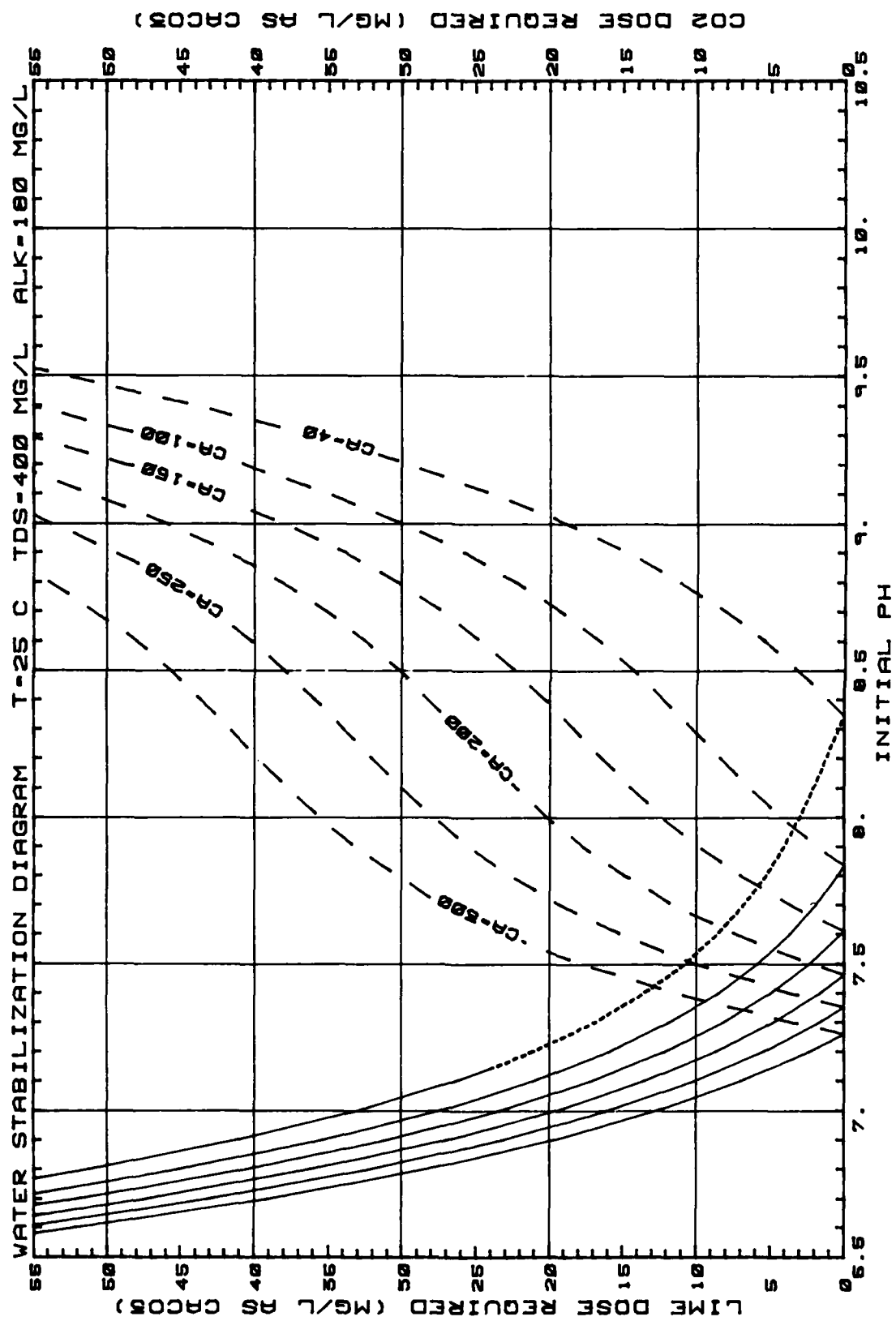


DIAGRAM A78

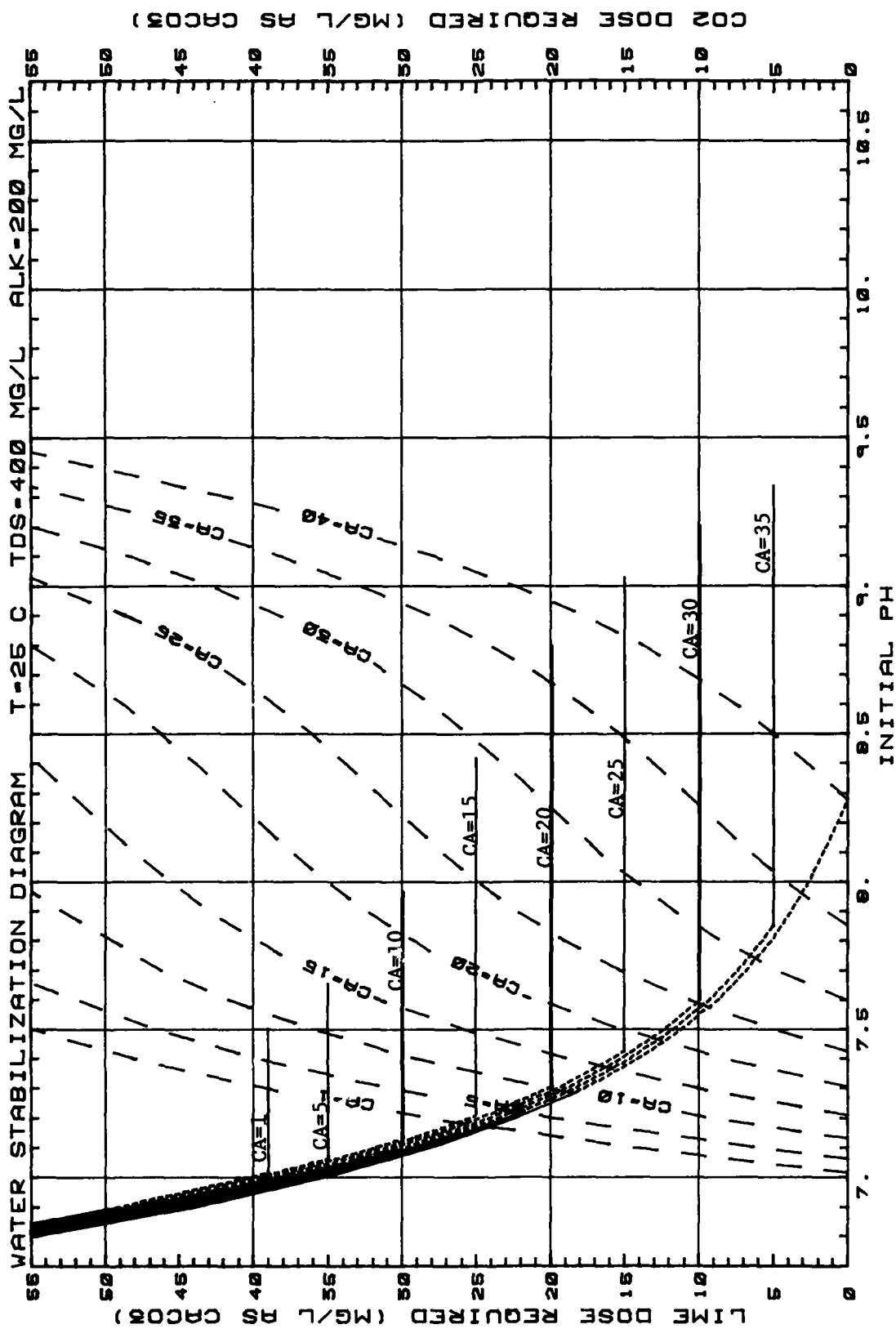


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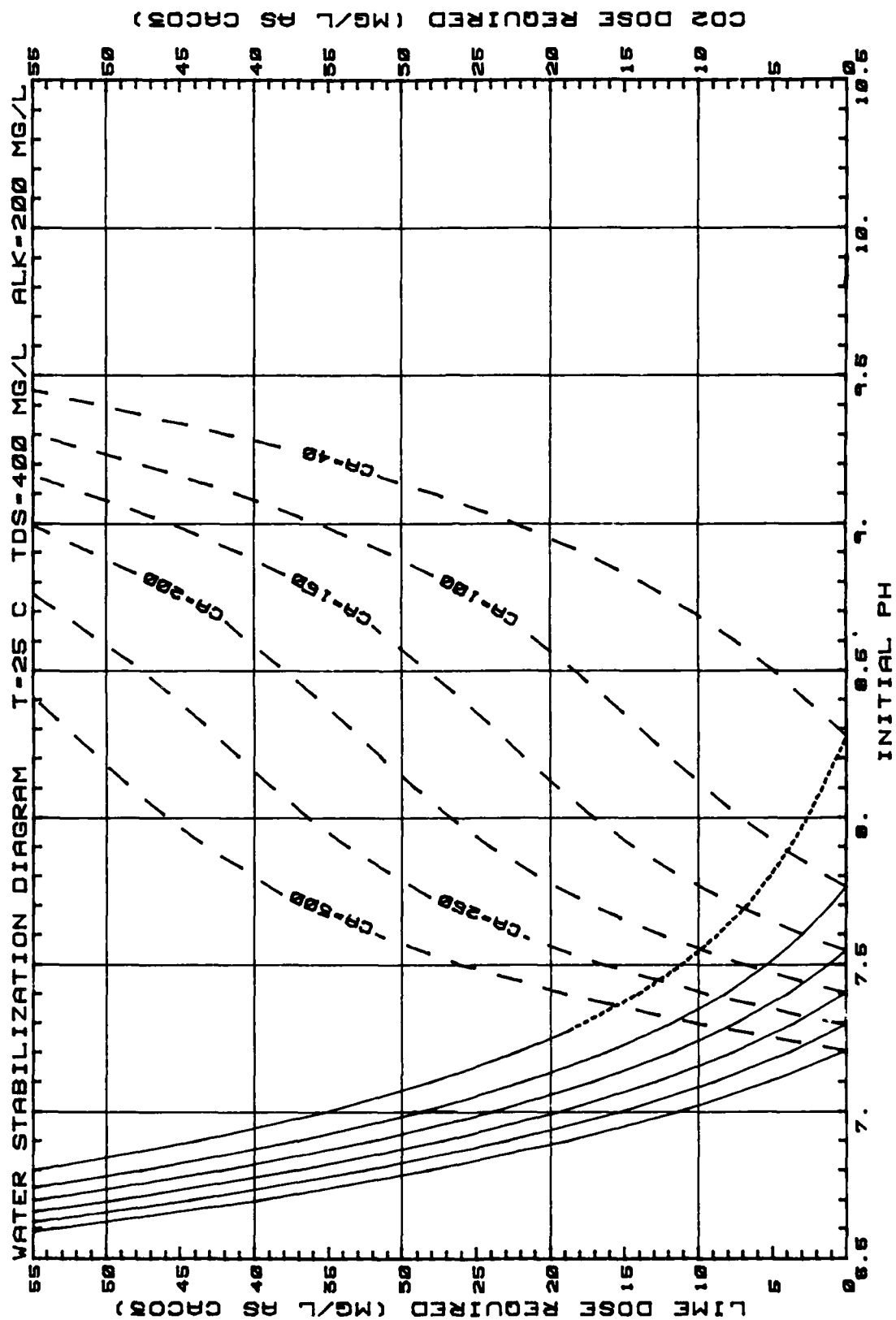


DIAGRAM A80

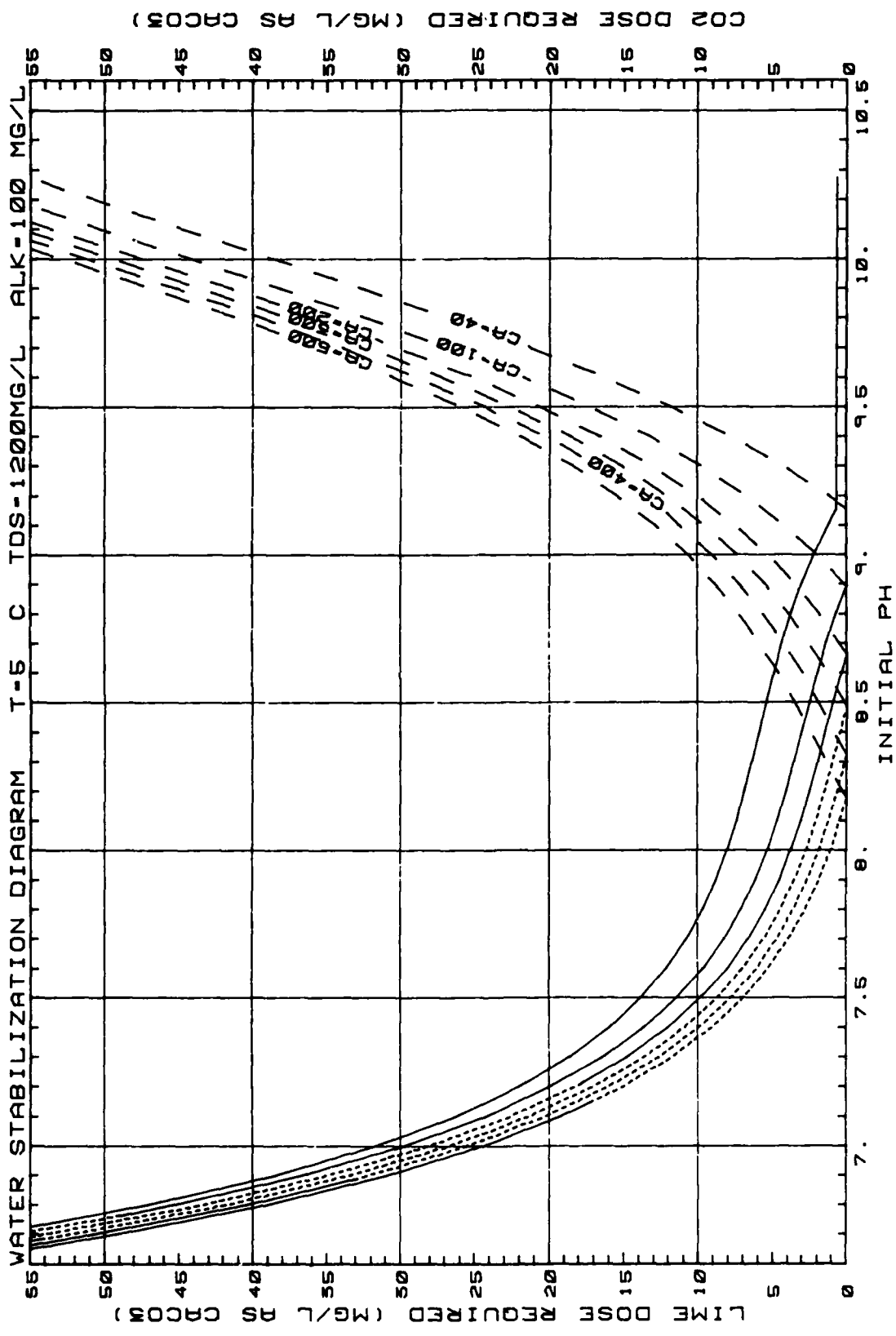


DIAGRAM A81

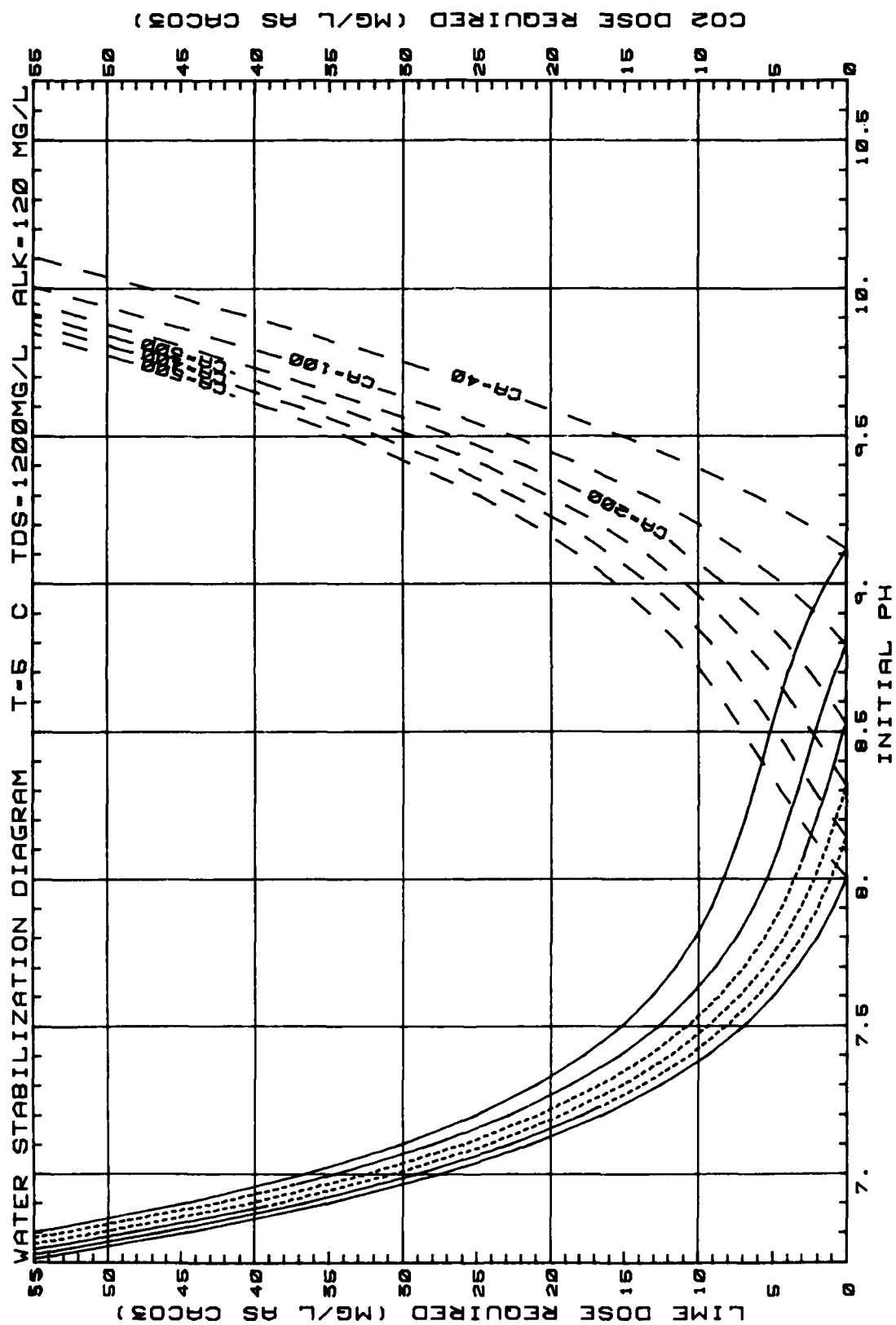


DIAGRAM A82

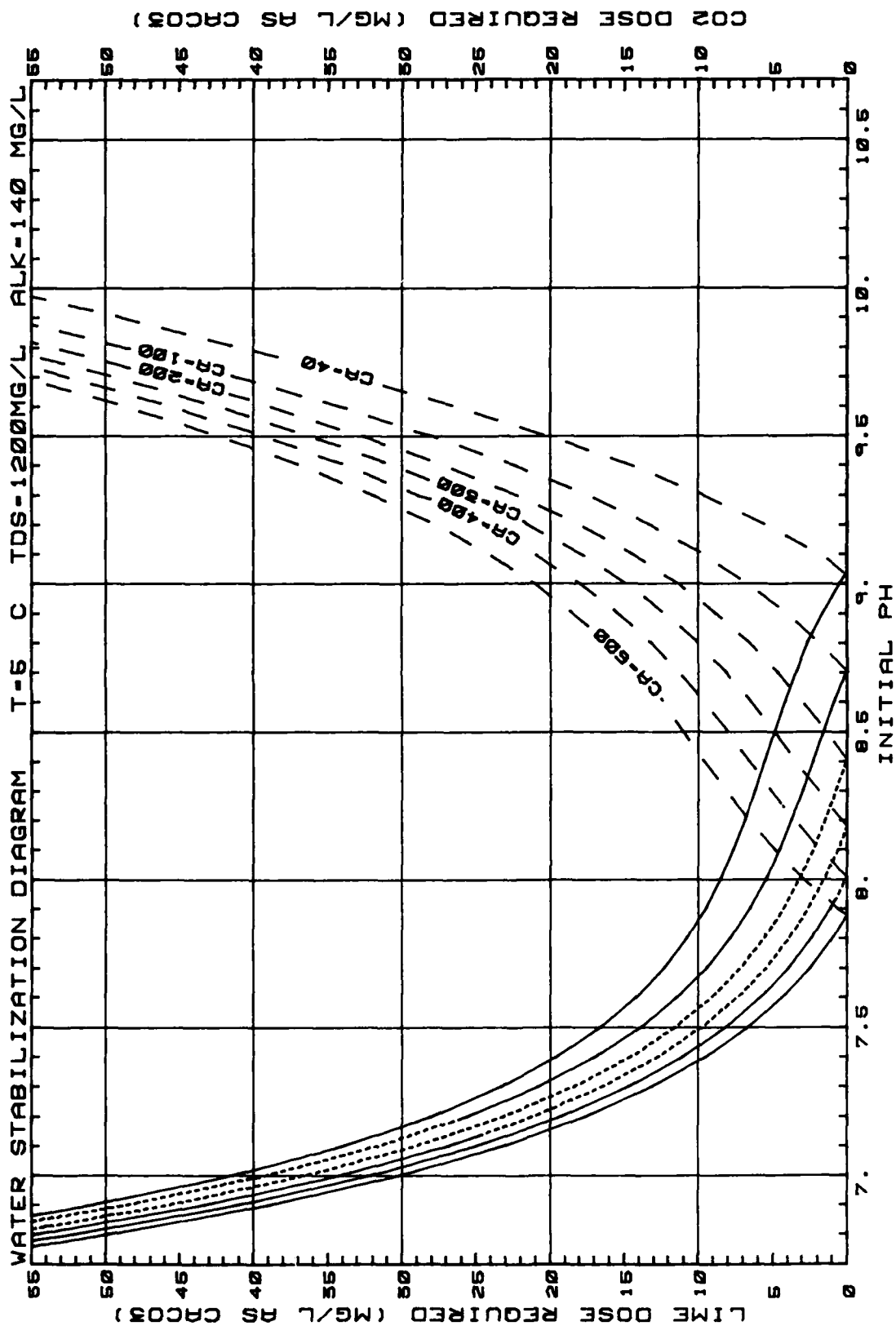


DIAGRAM A83

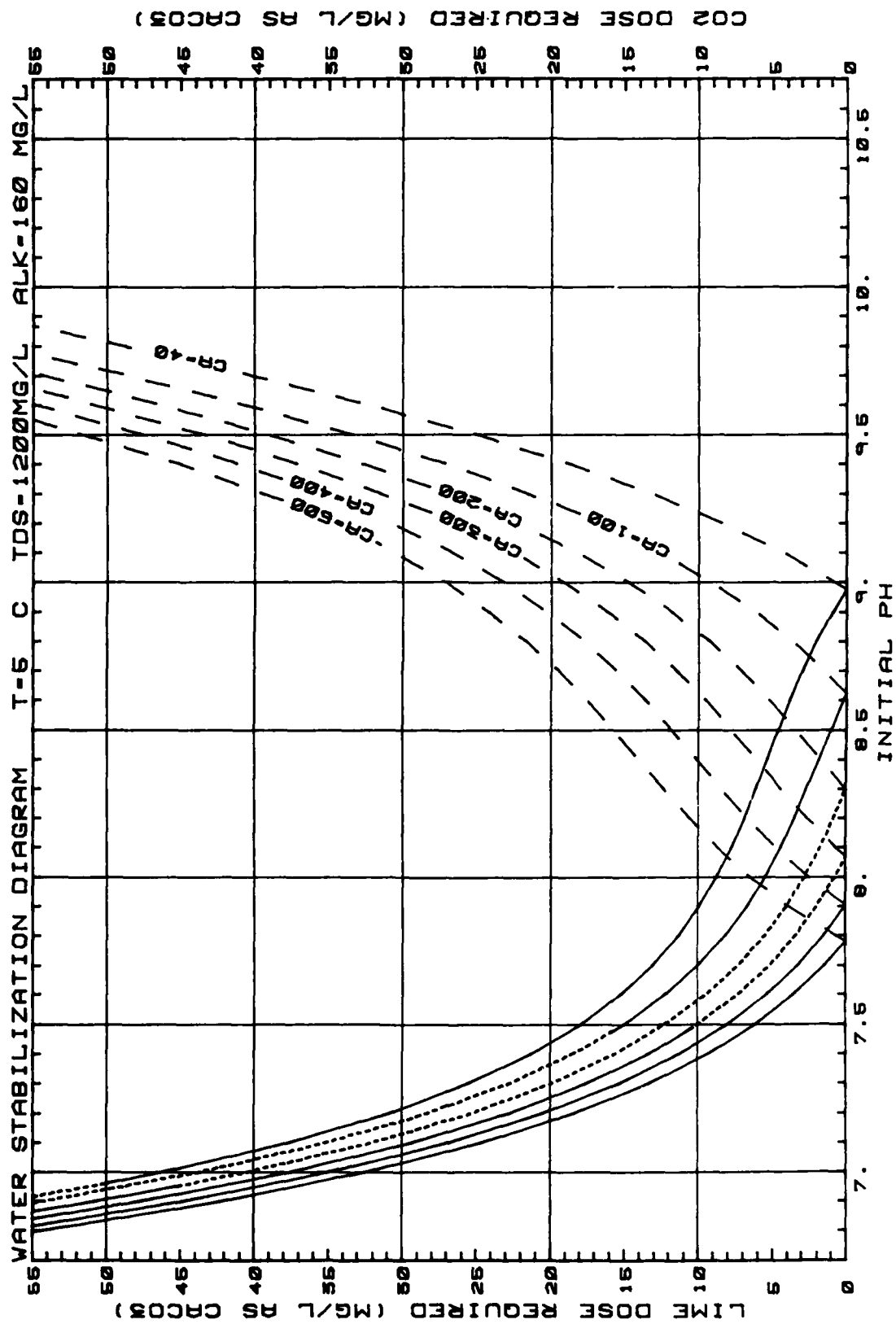


DIAGRAM A84

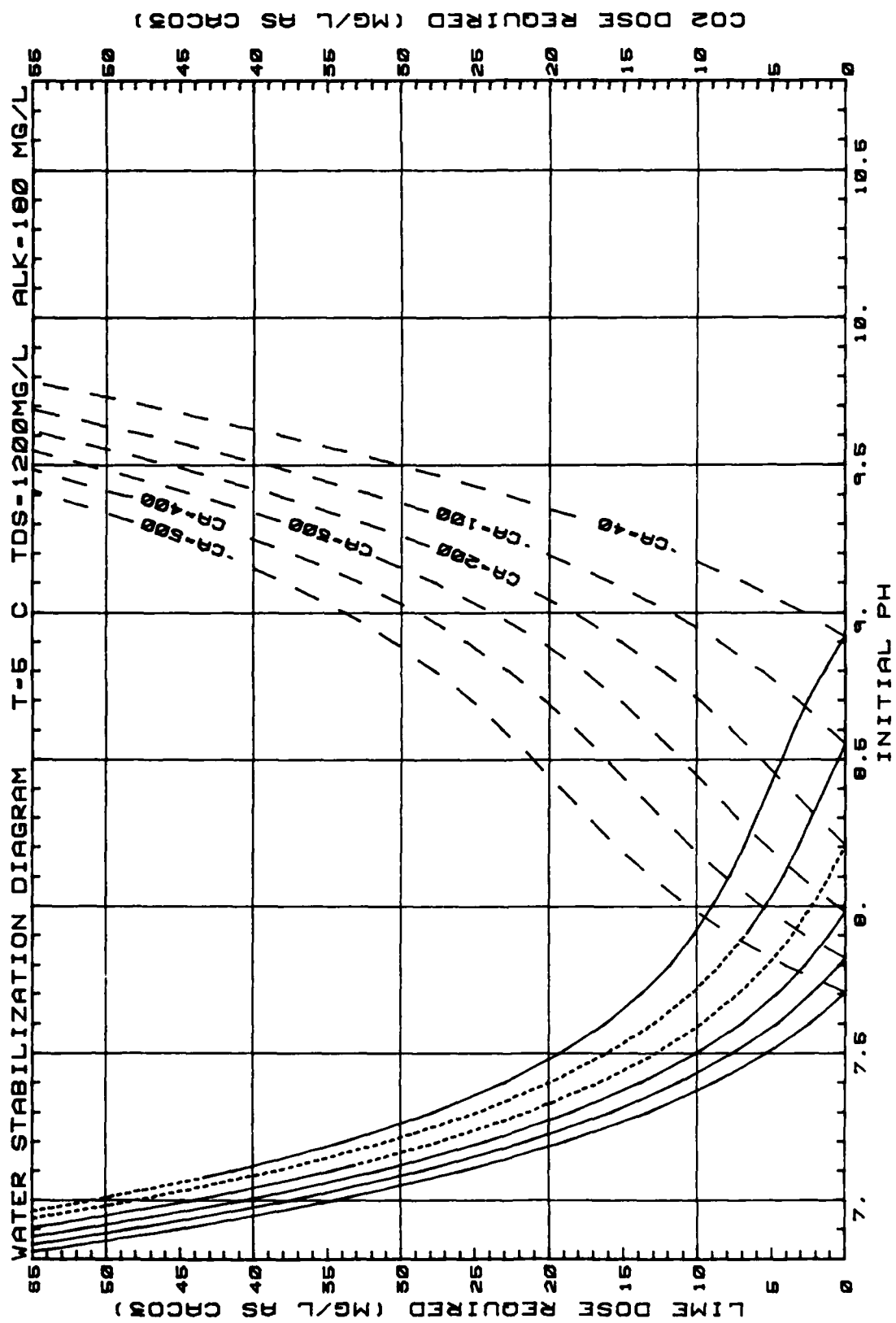


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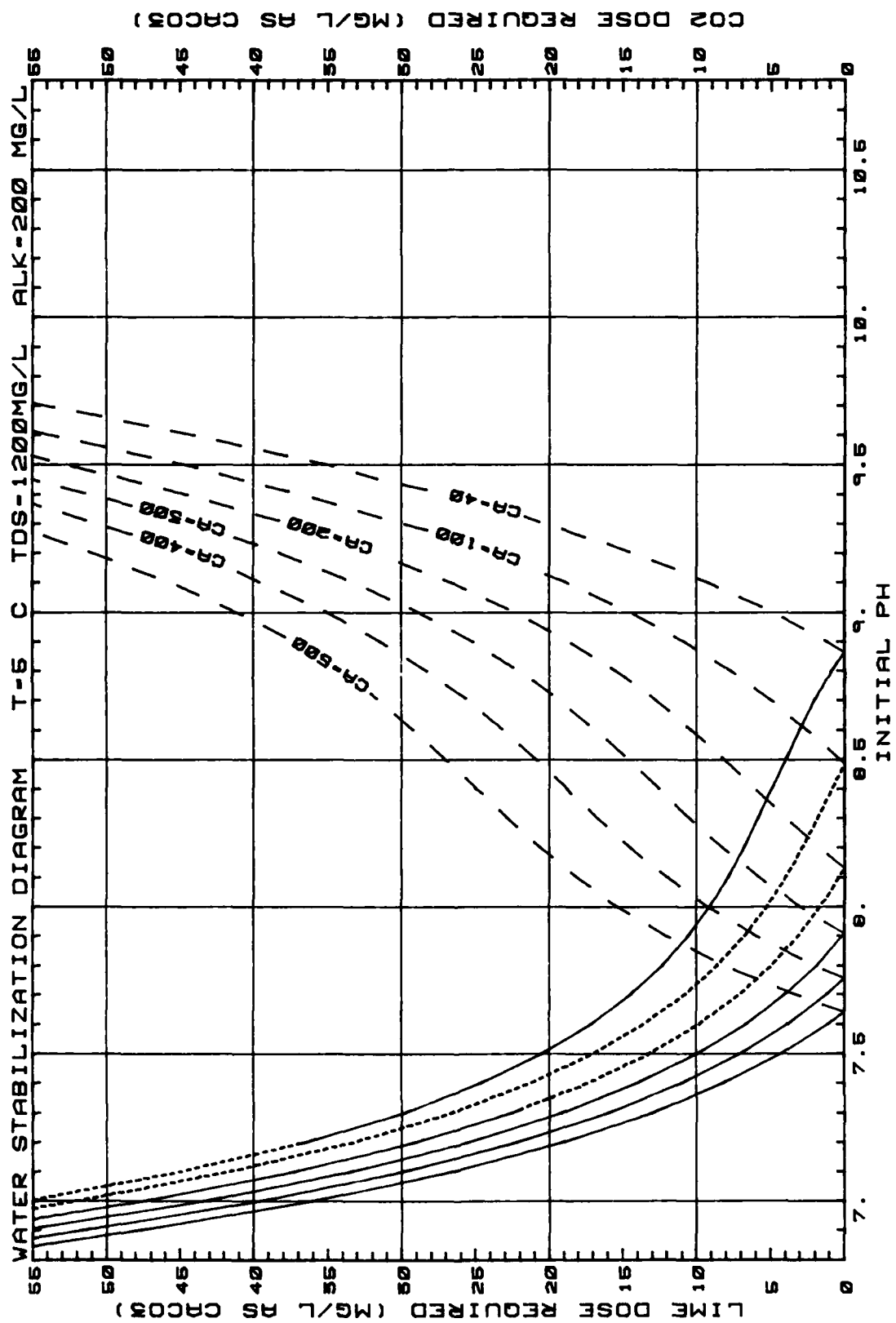


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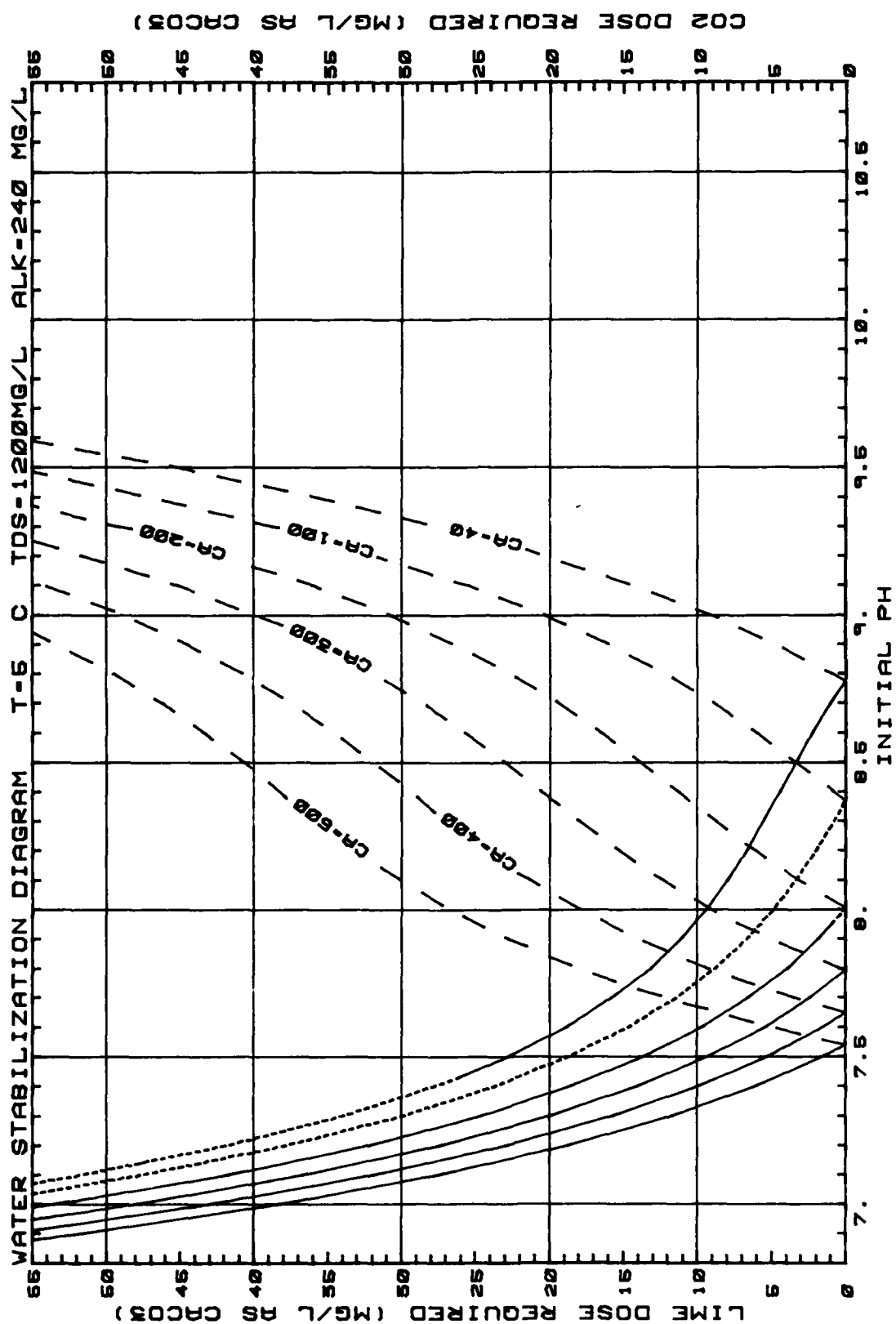


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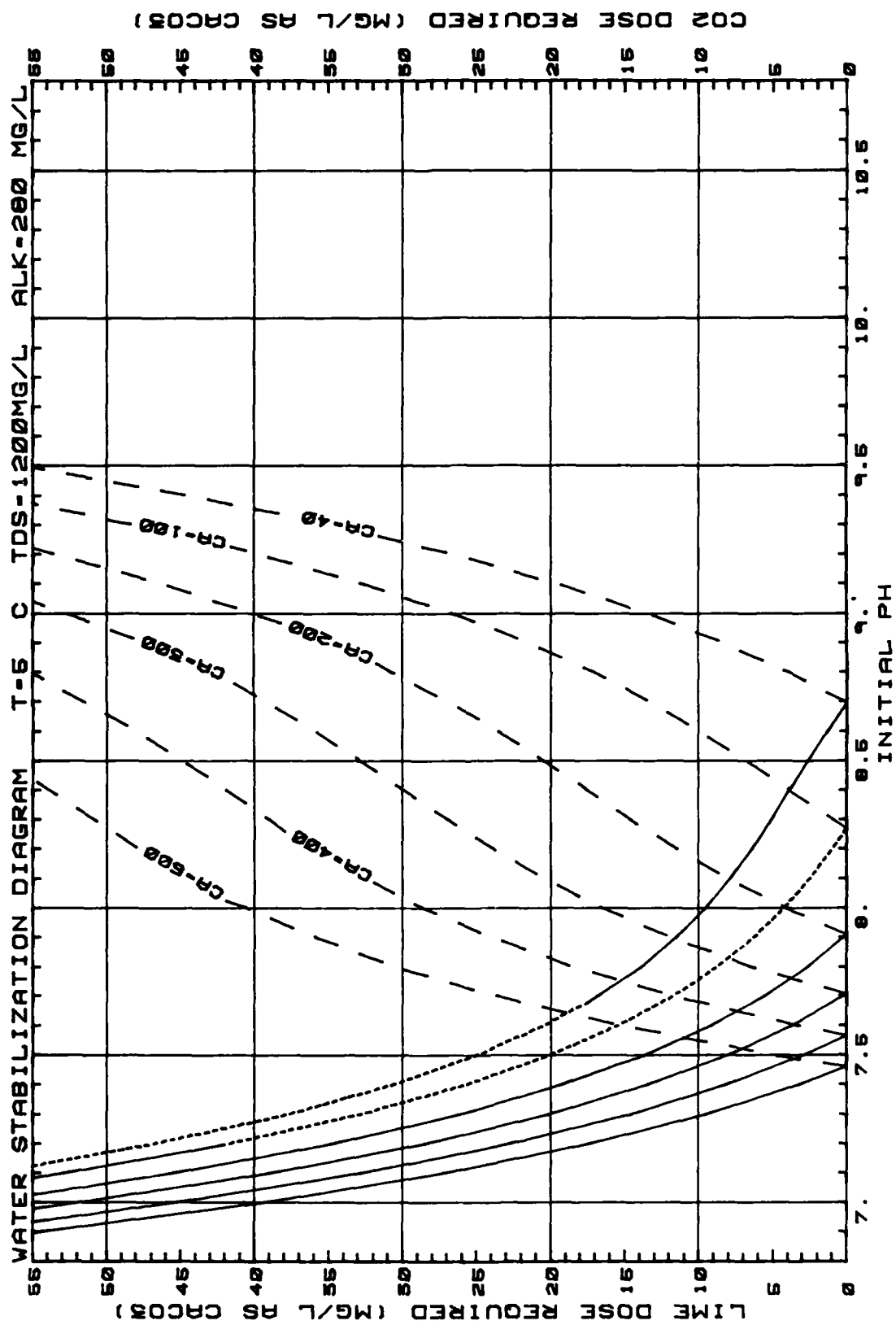


DIAGRAM A88

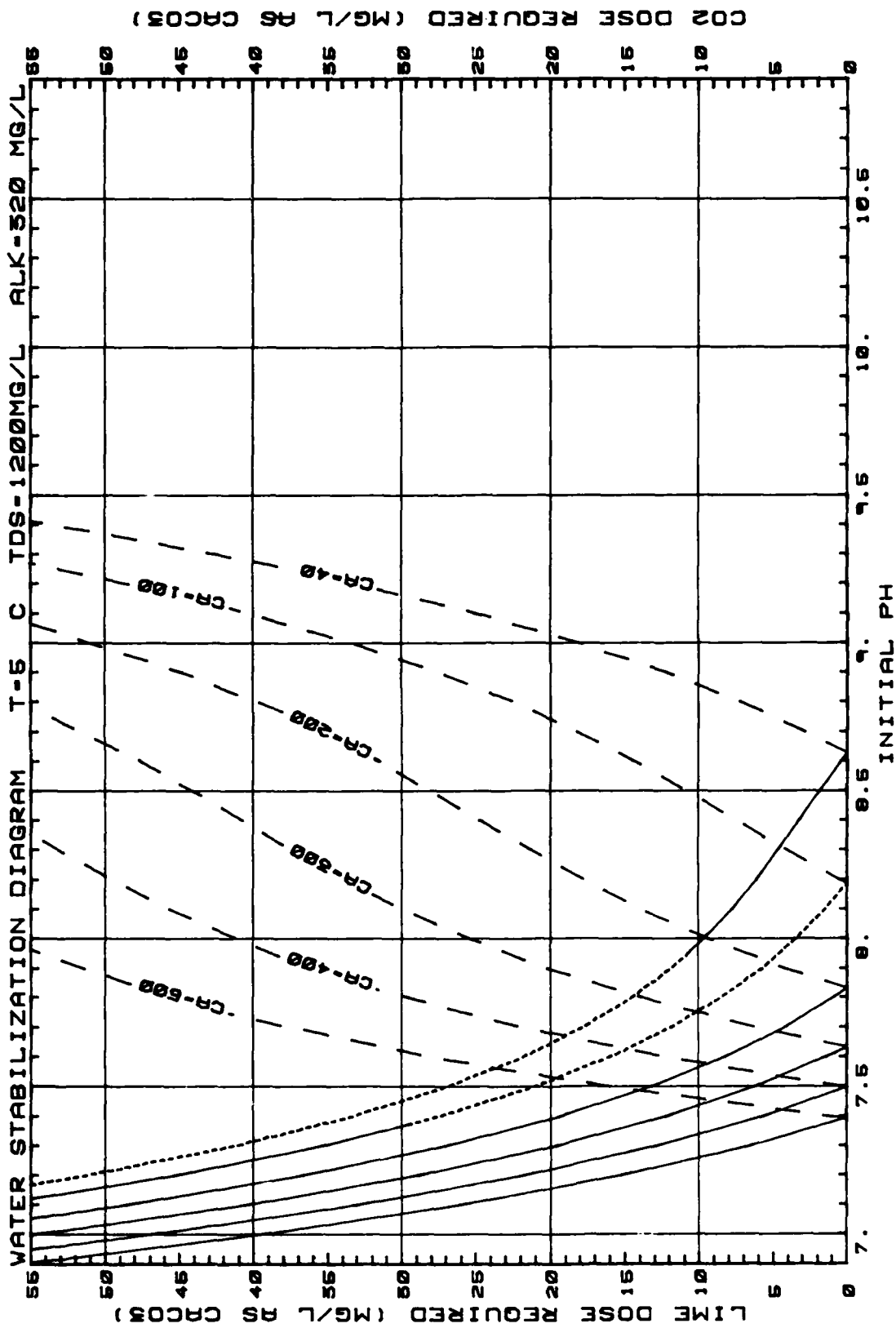


DIAGRAM A89

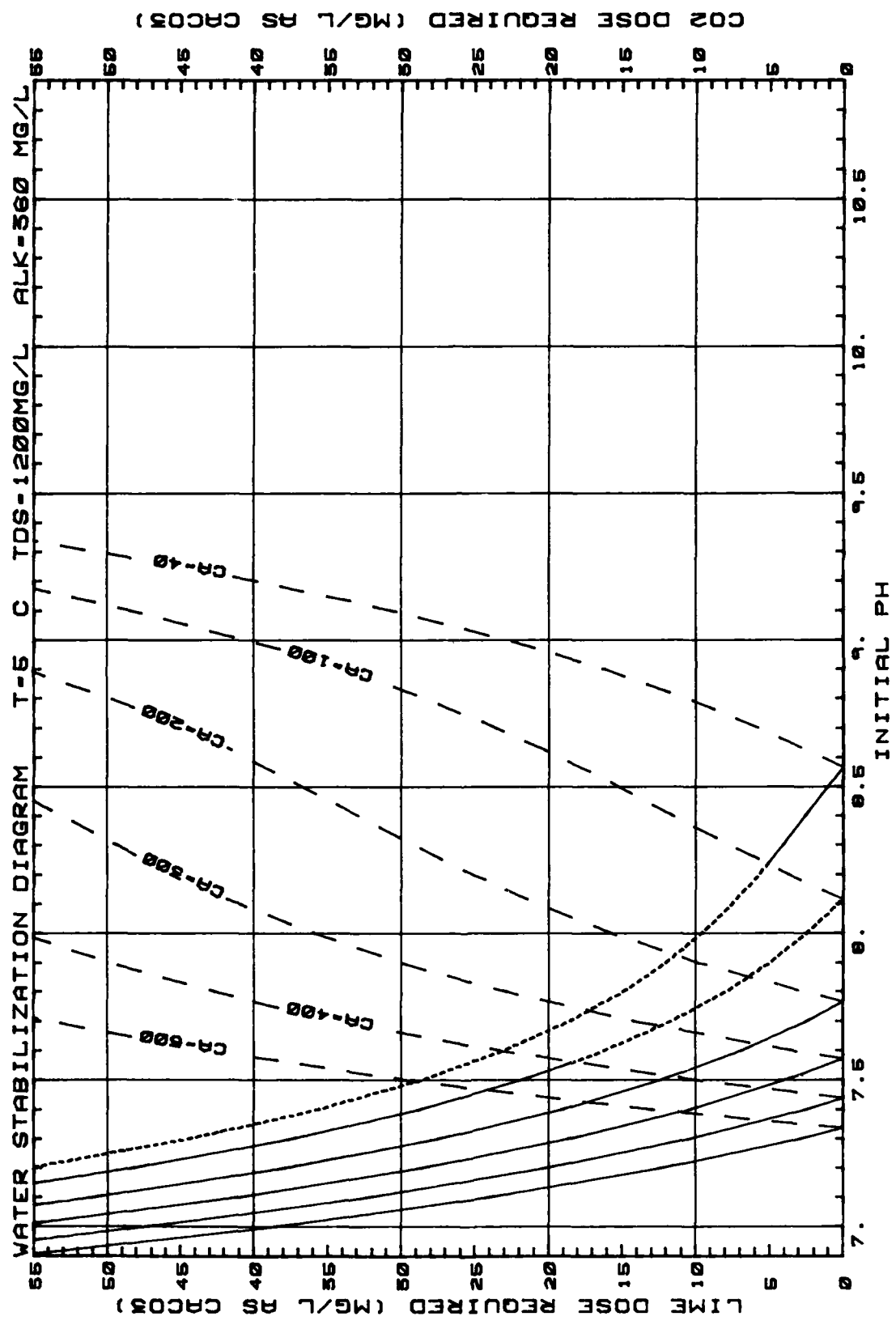


DIAGRAM A90

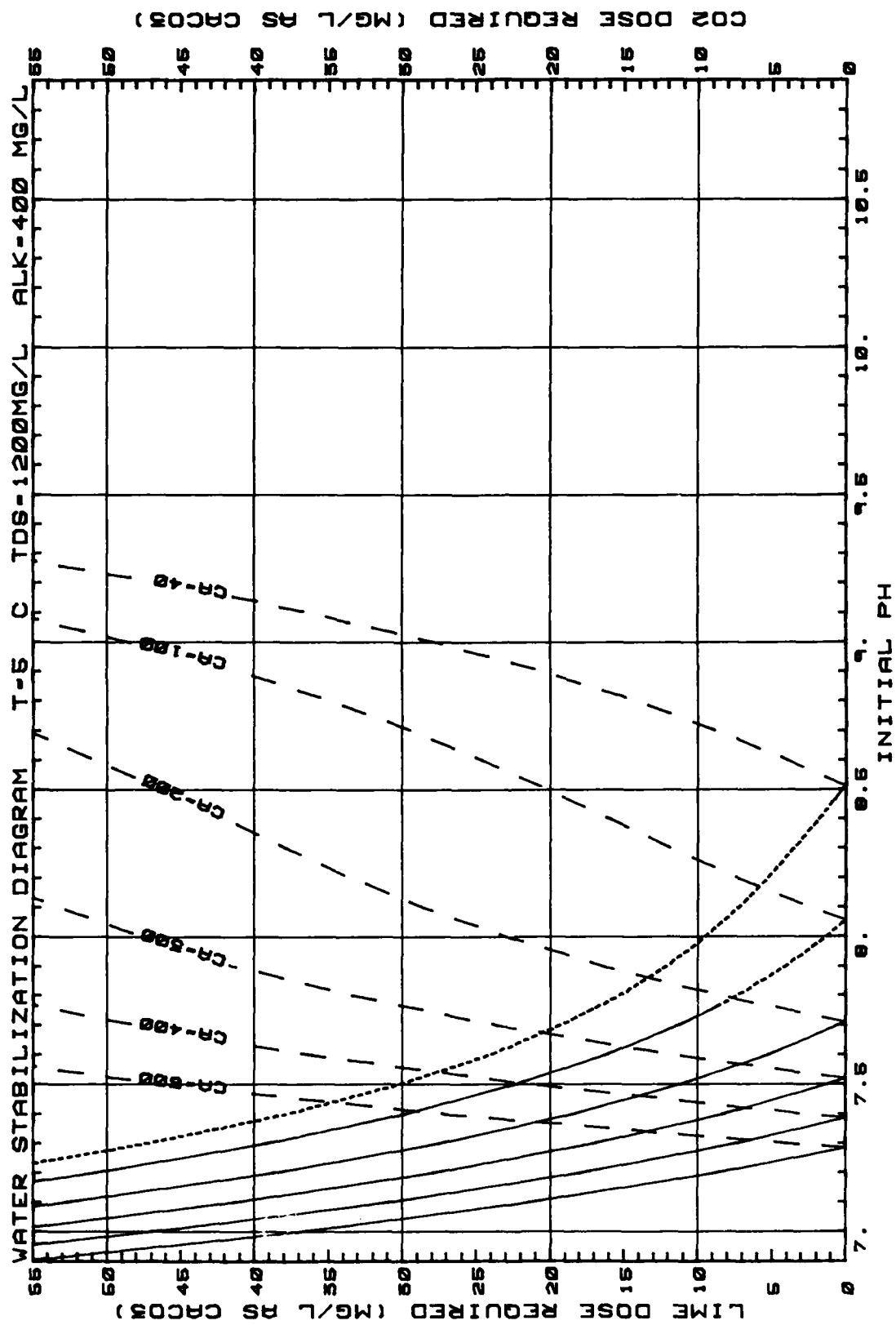


DIAGRAM A91

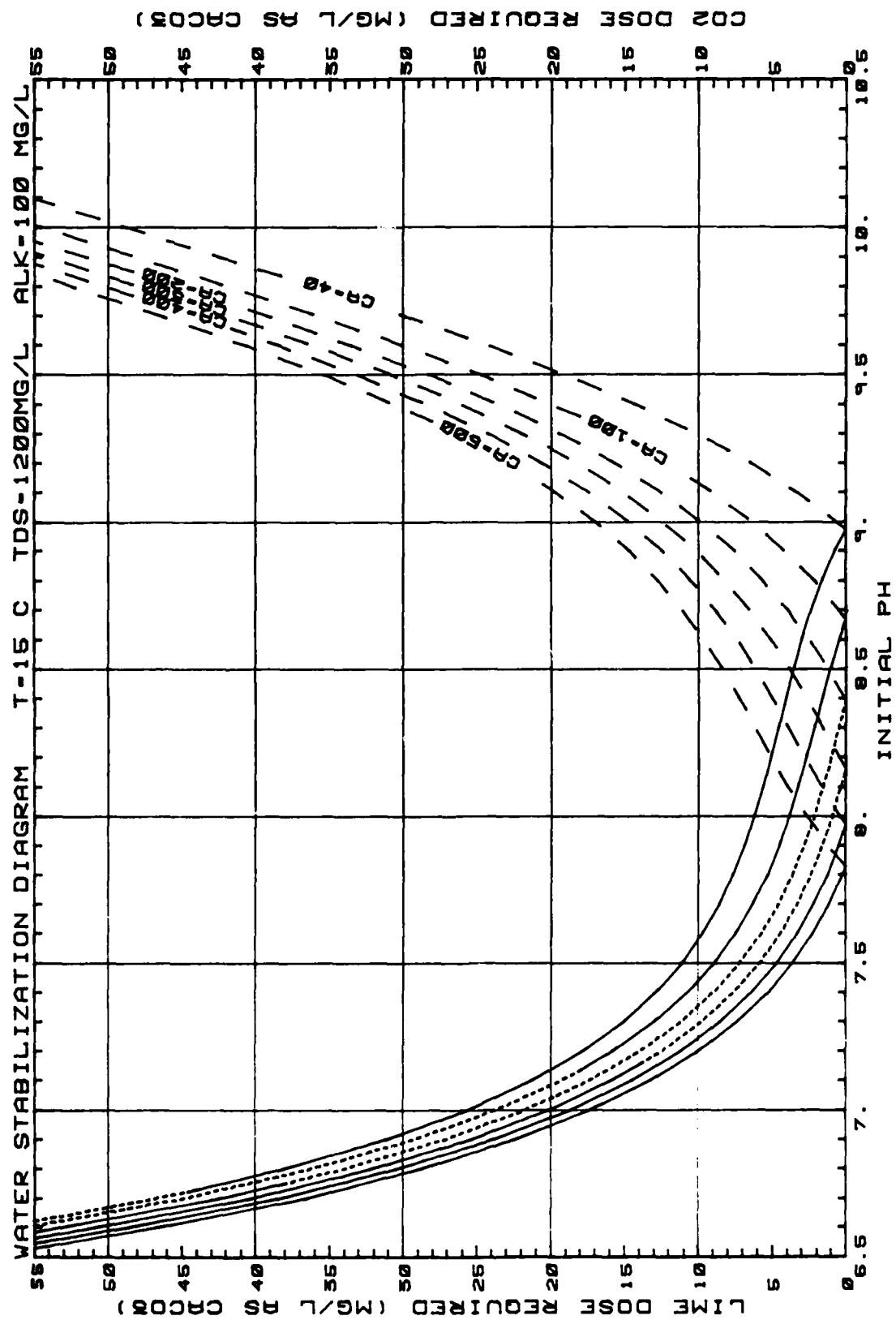


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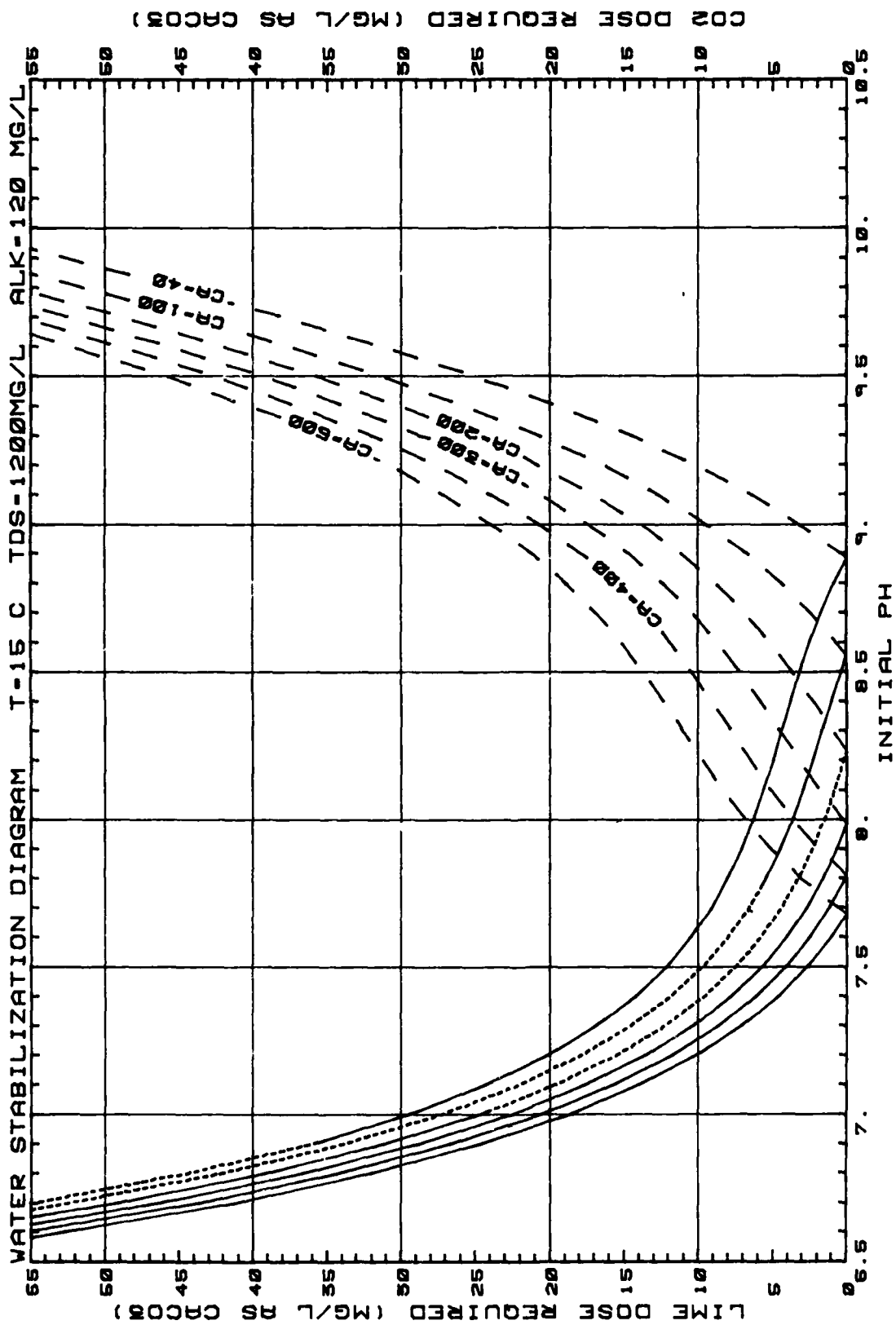


DIAGRAM A93

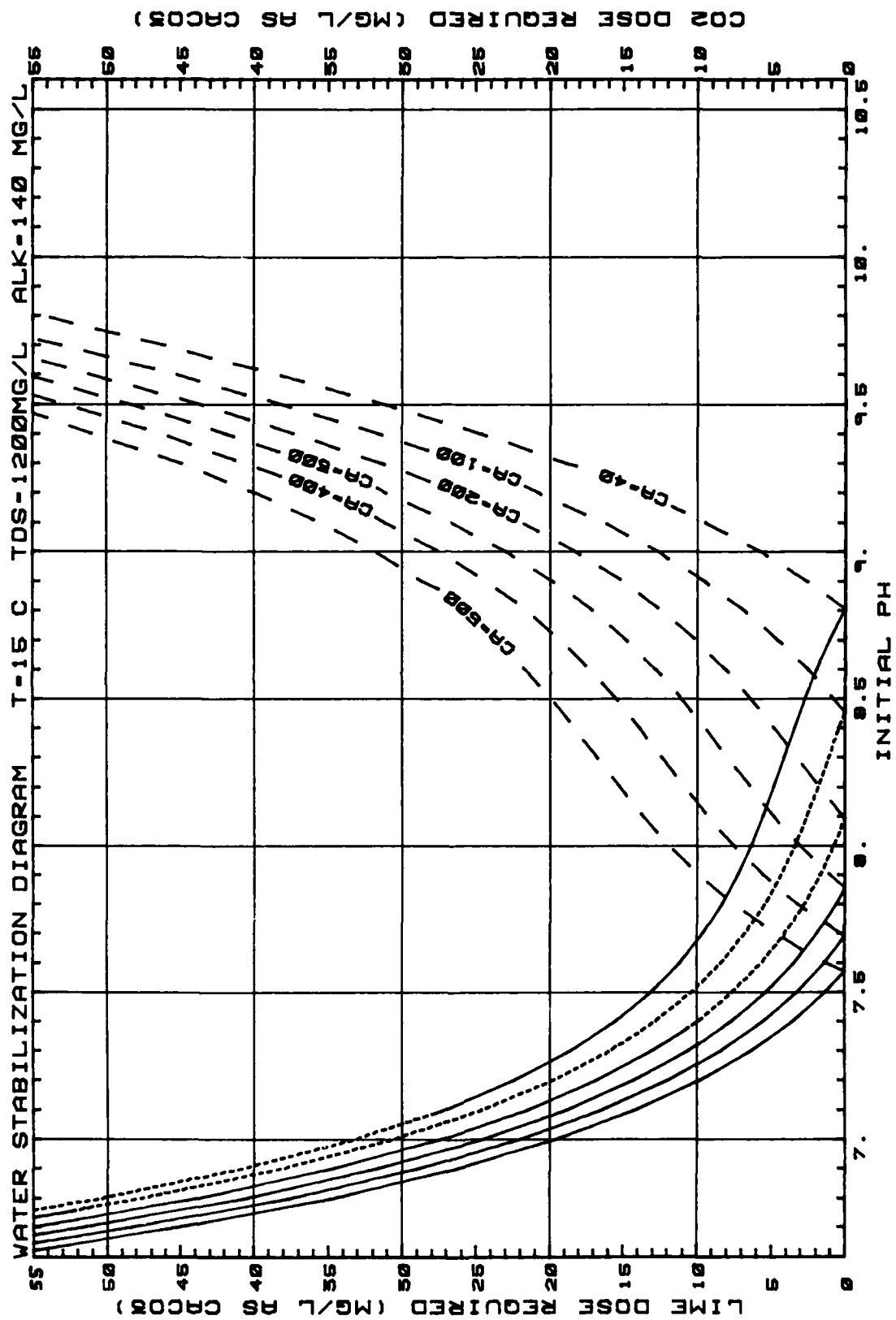


DIAGRAM A94

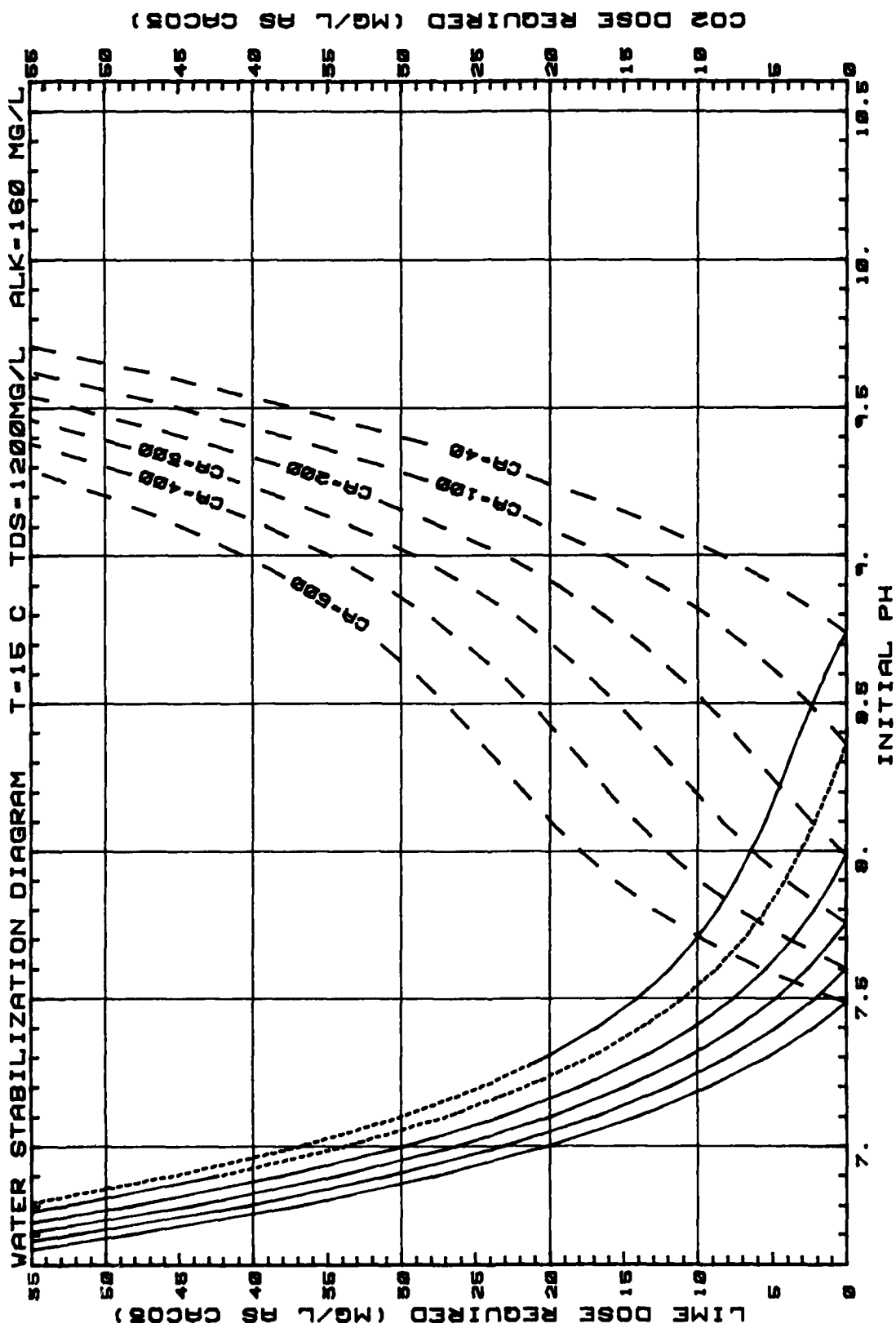


DIAGRAM A95

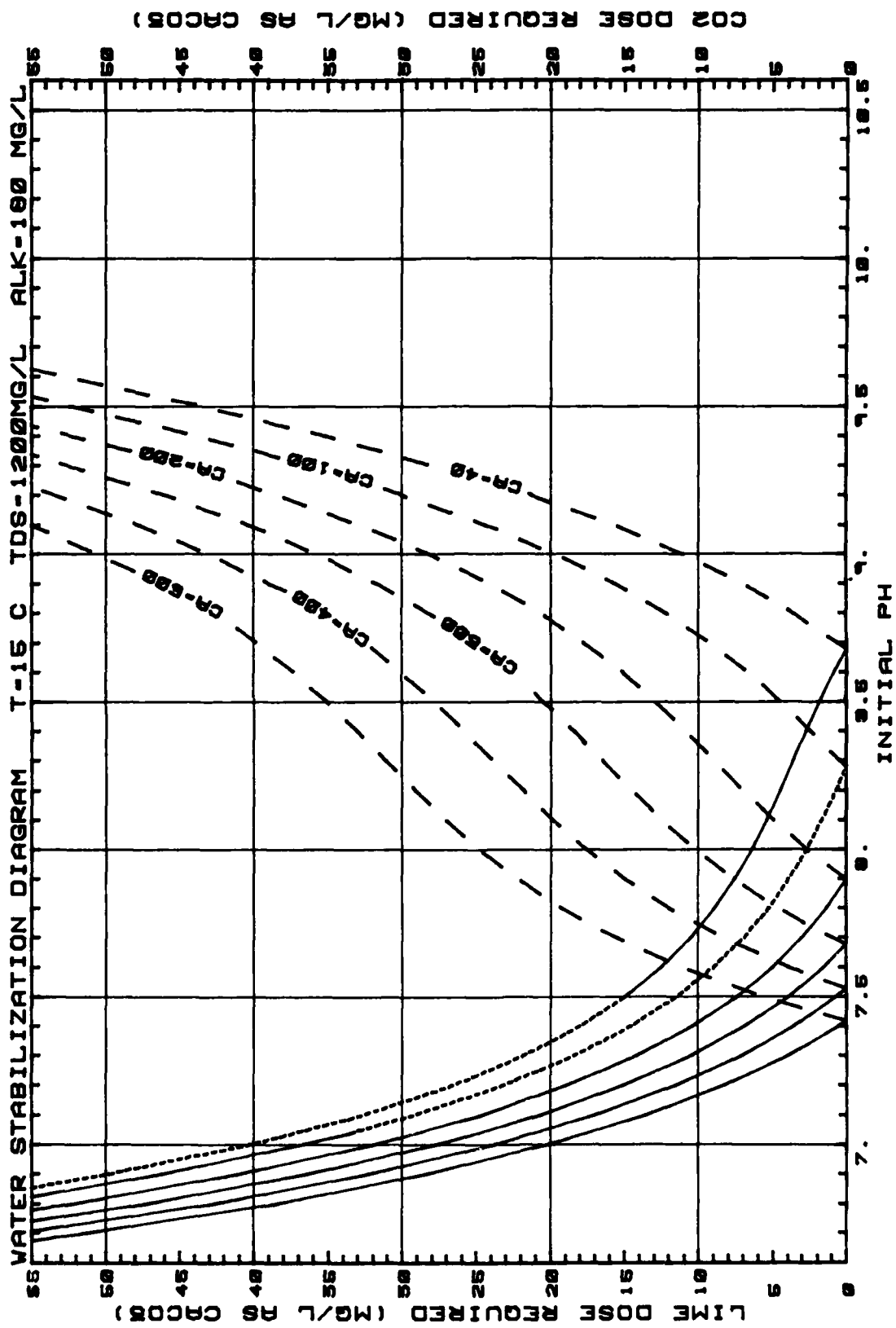


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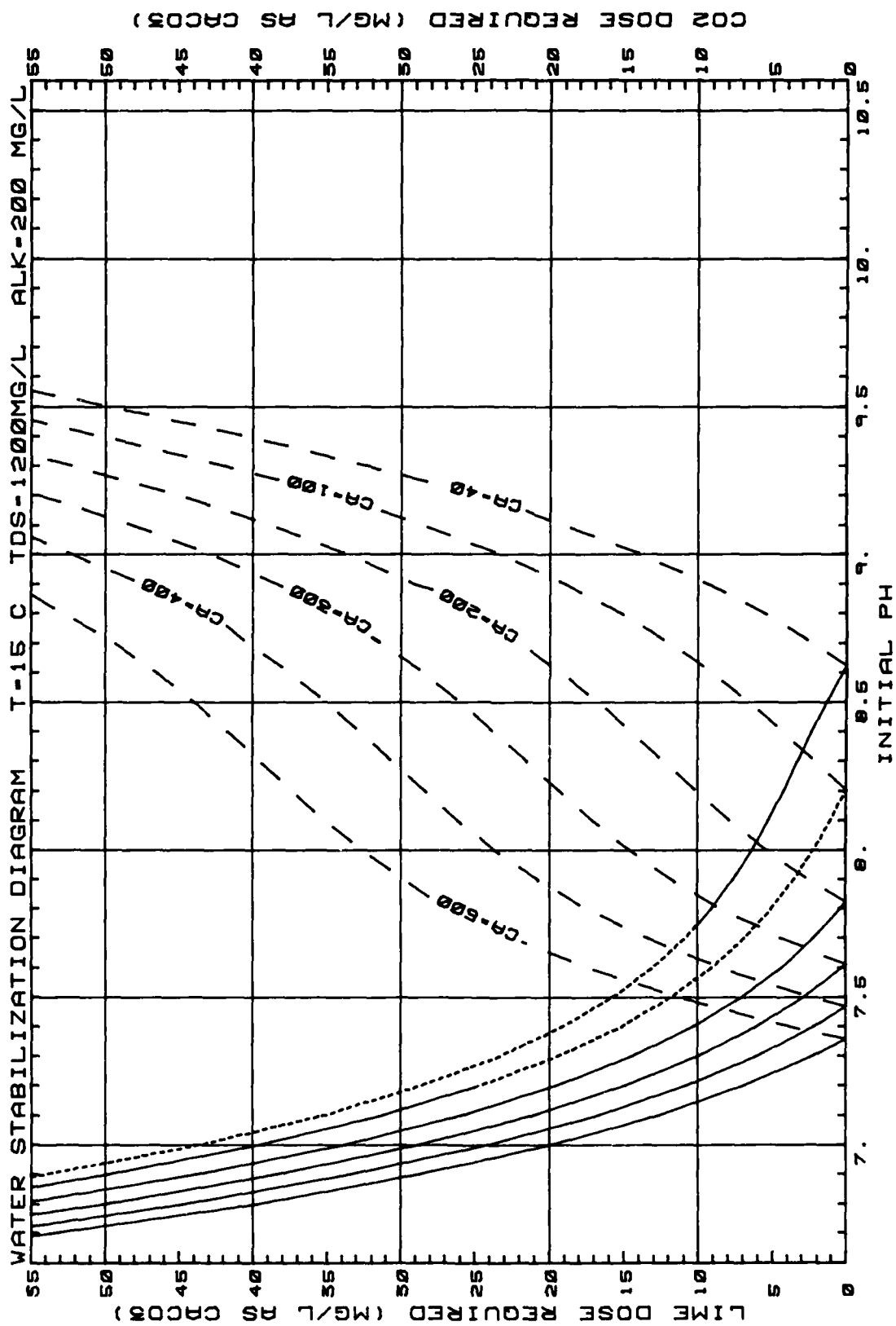


DIAGRAM A97

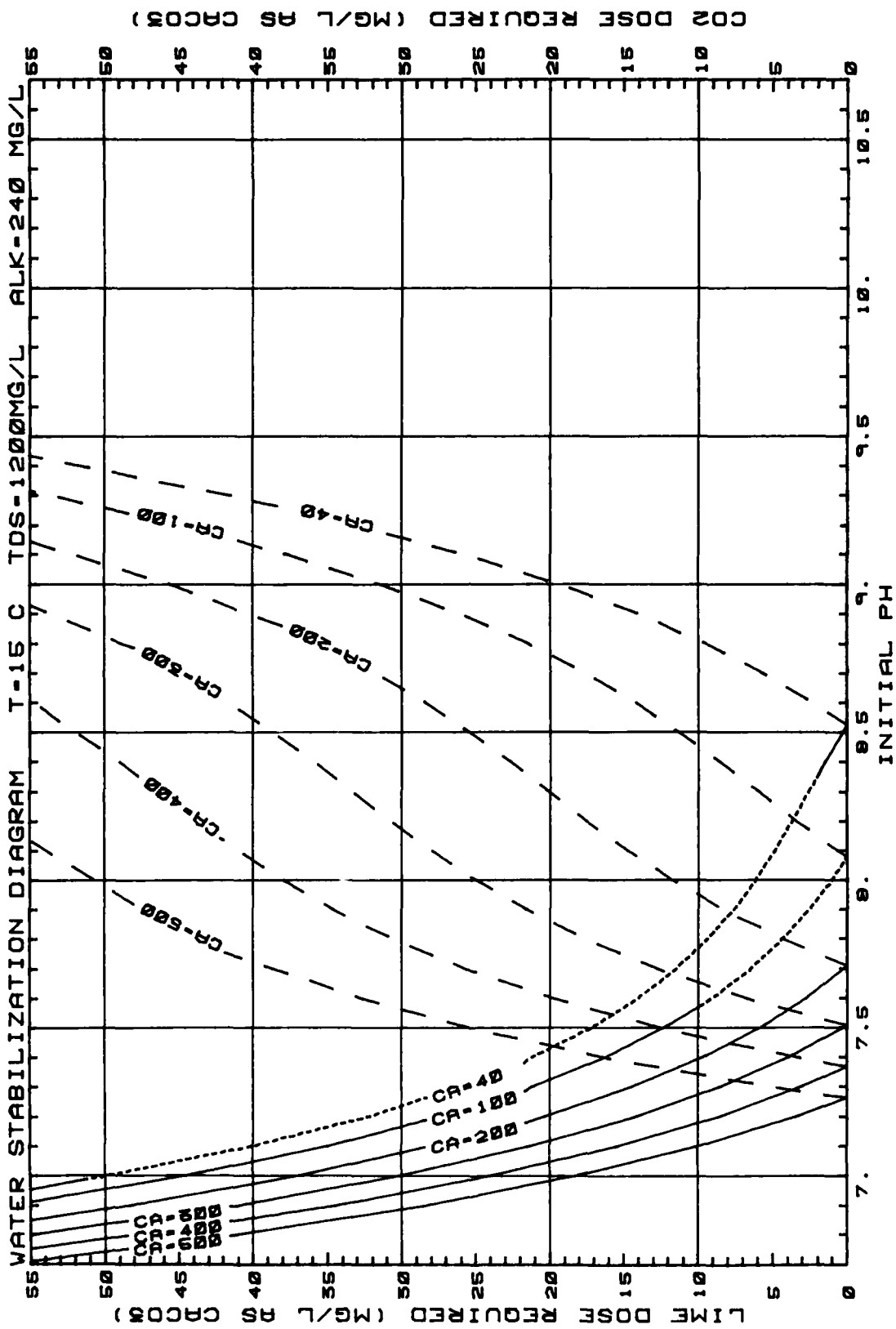


DIAGRAM A98

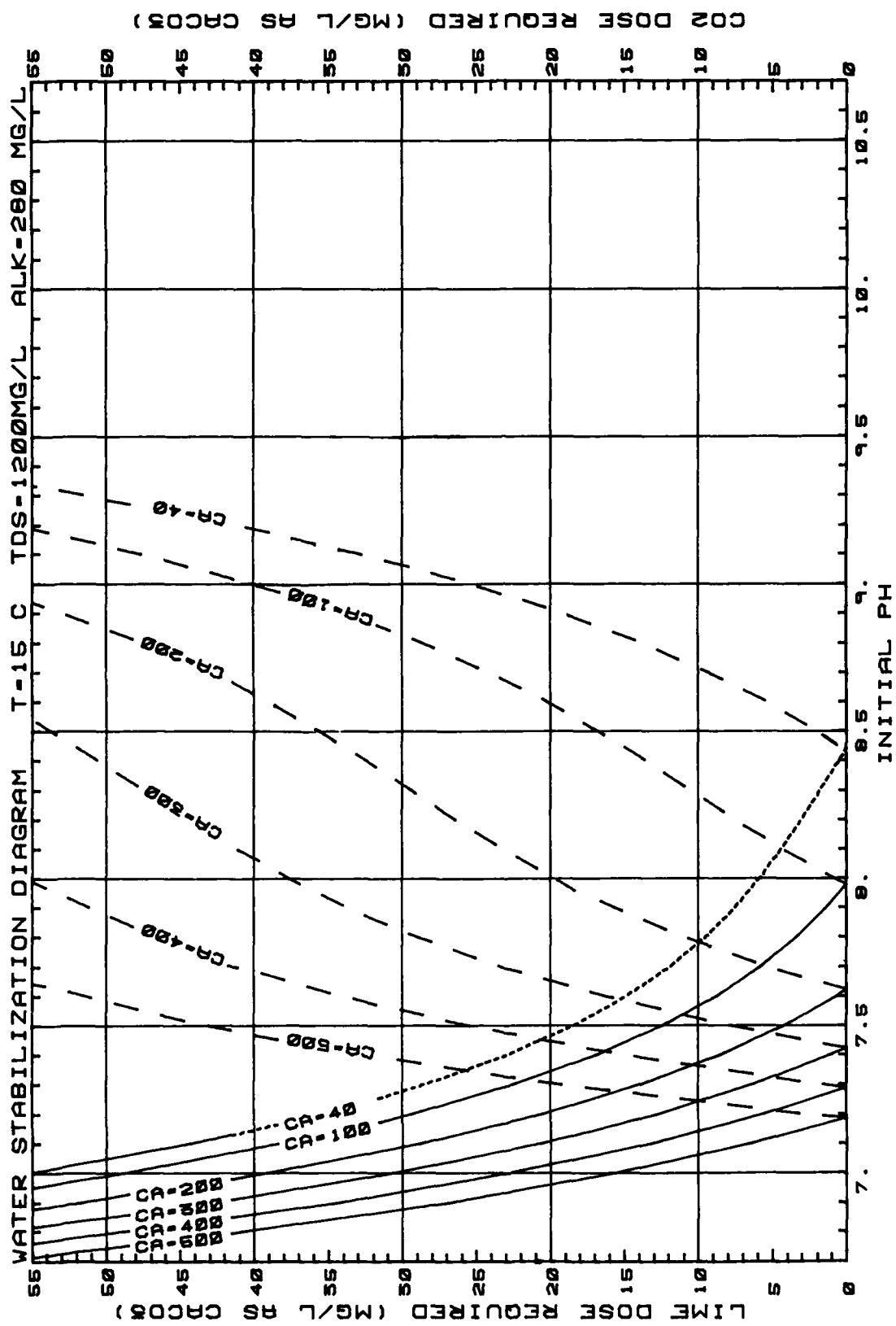


DIAGRAM A99

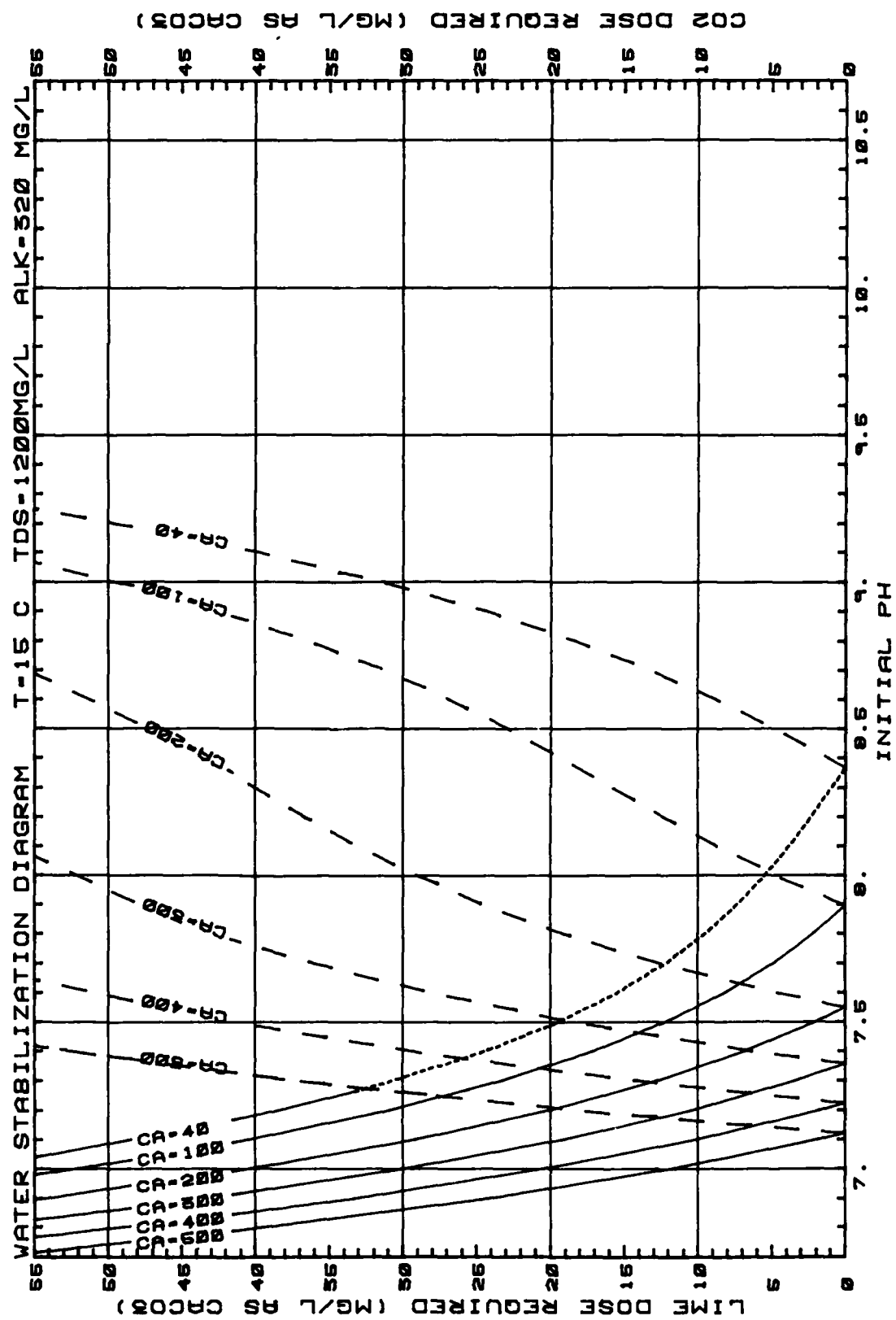


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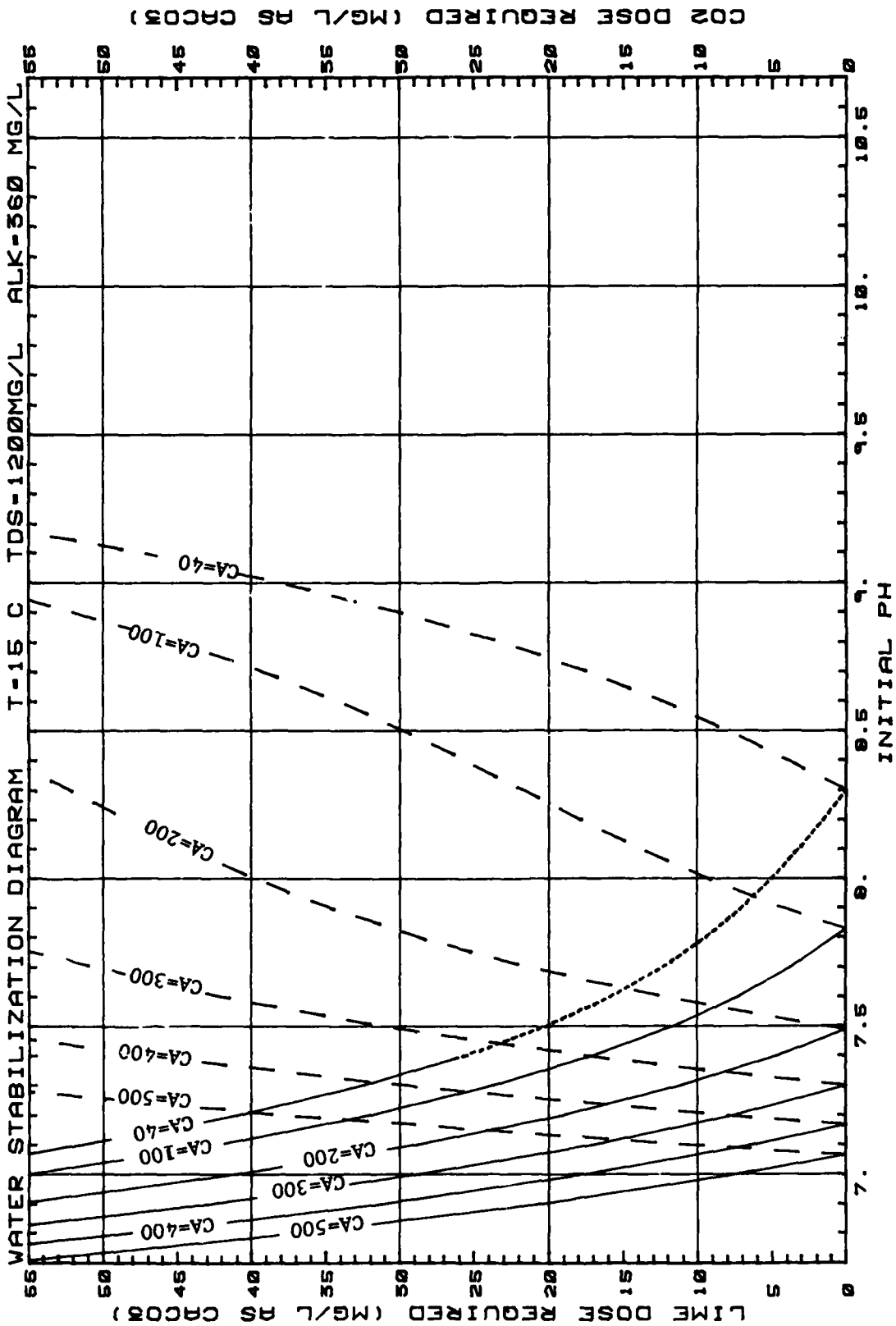


DIAGRAM A101

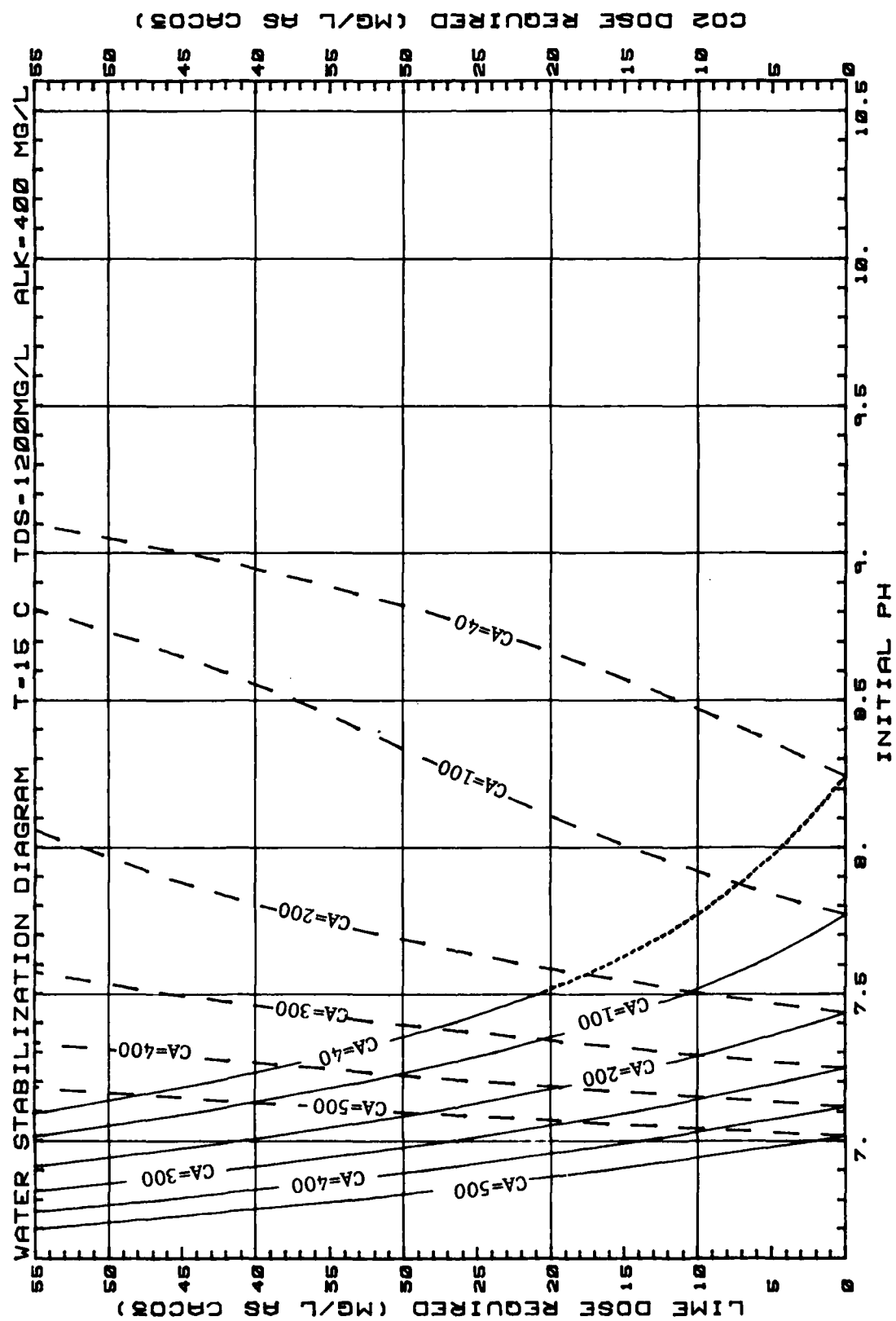


DIAGRAM A102

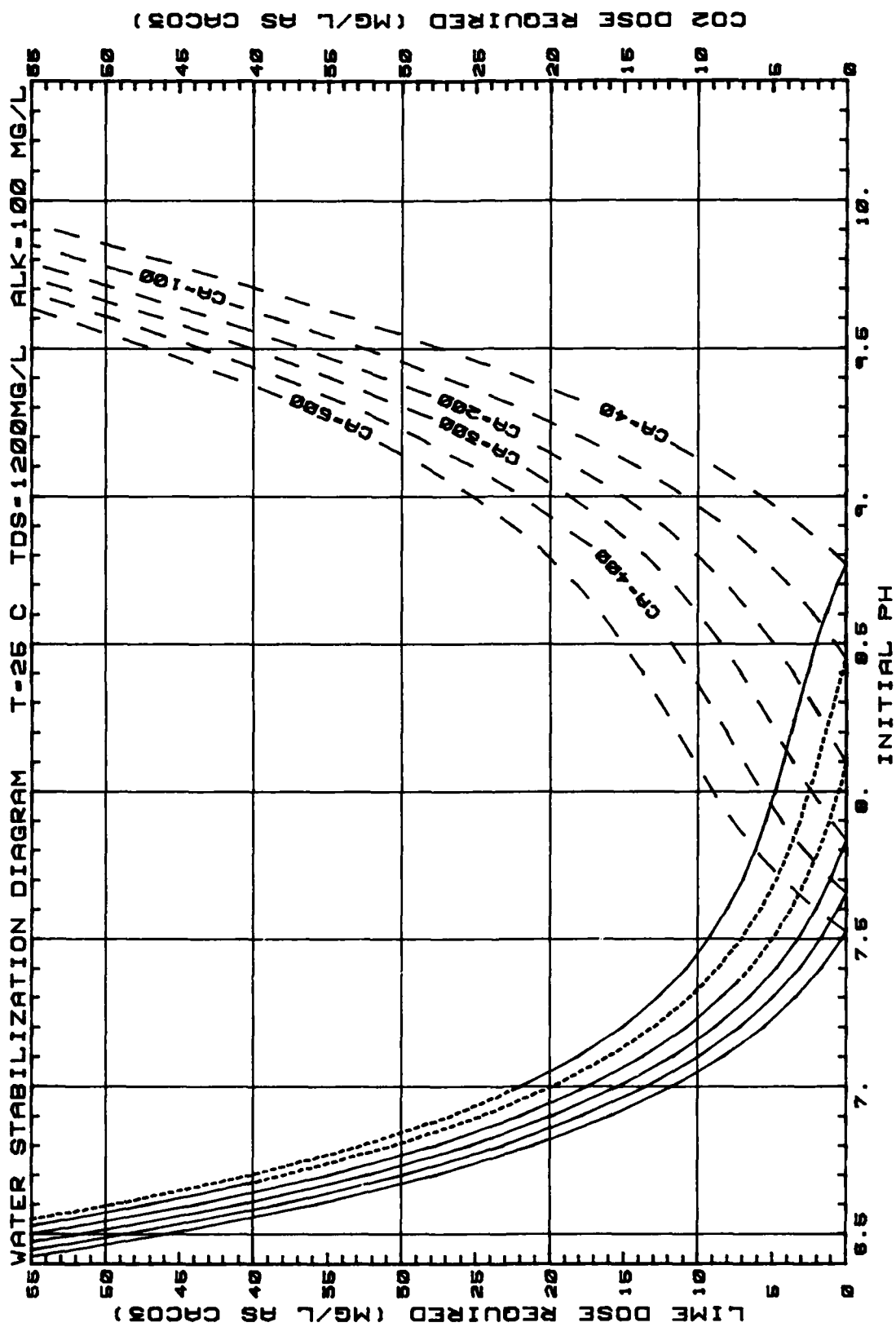


DIAGRAM A103



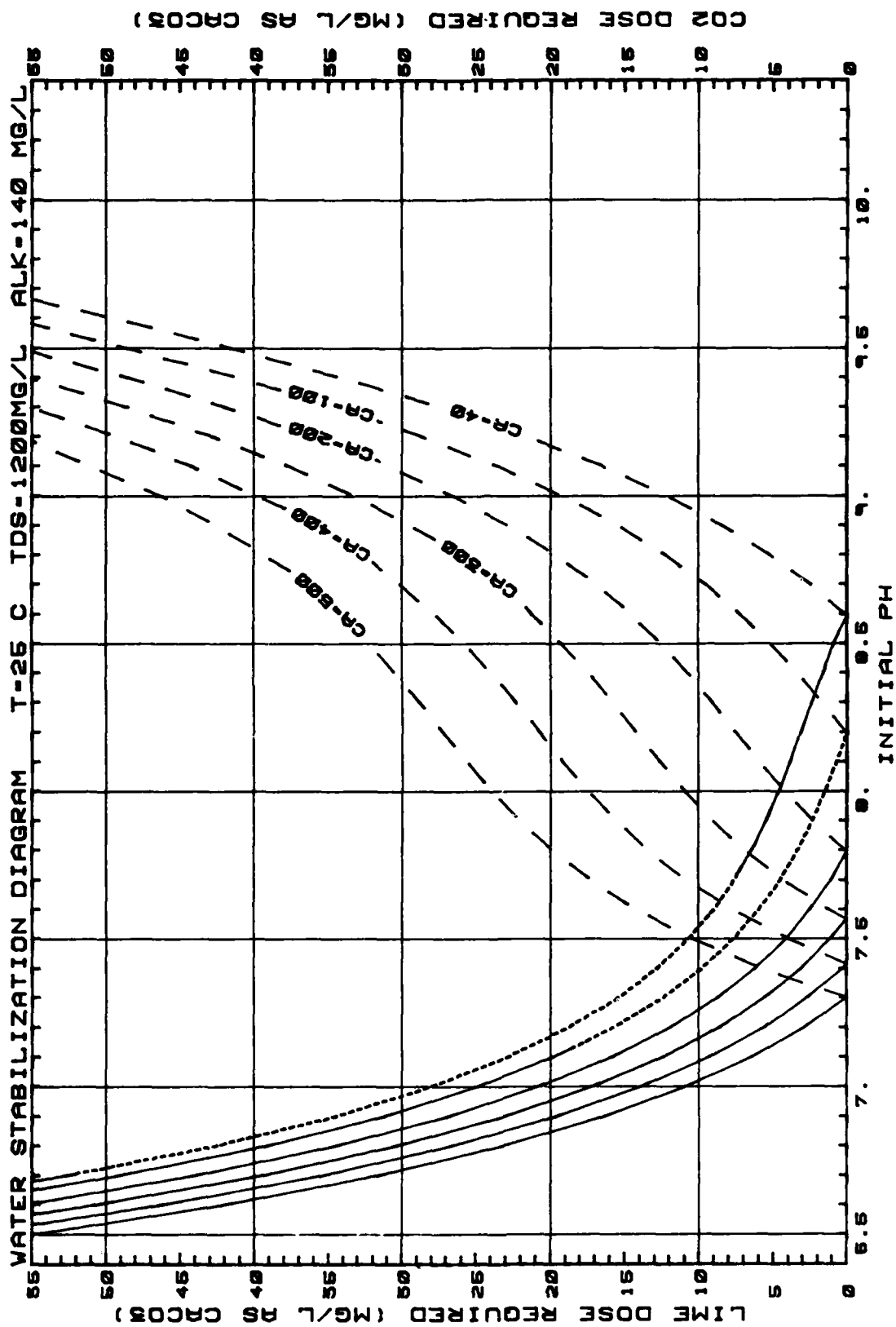


DIAGRAM A105

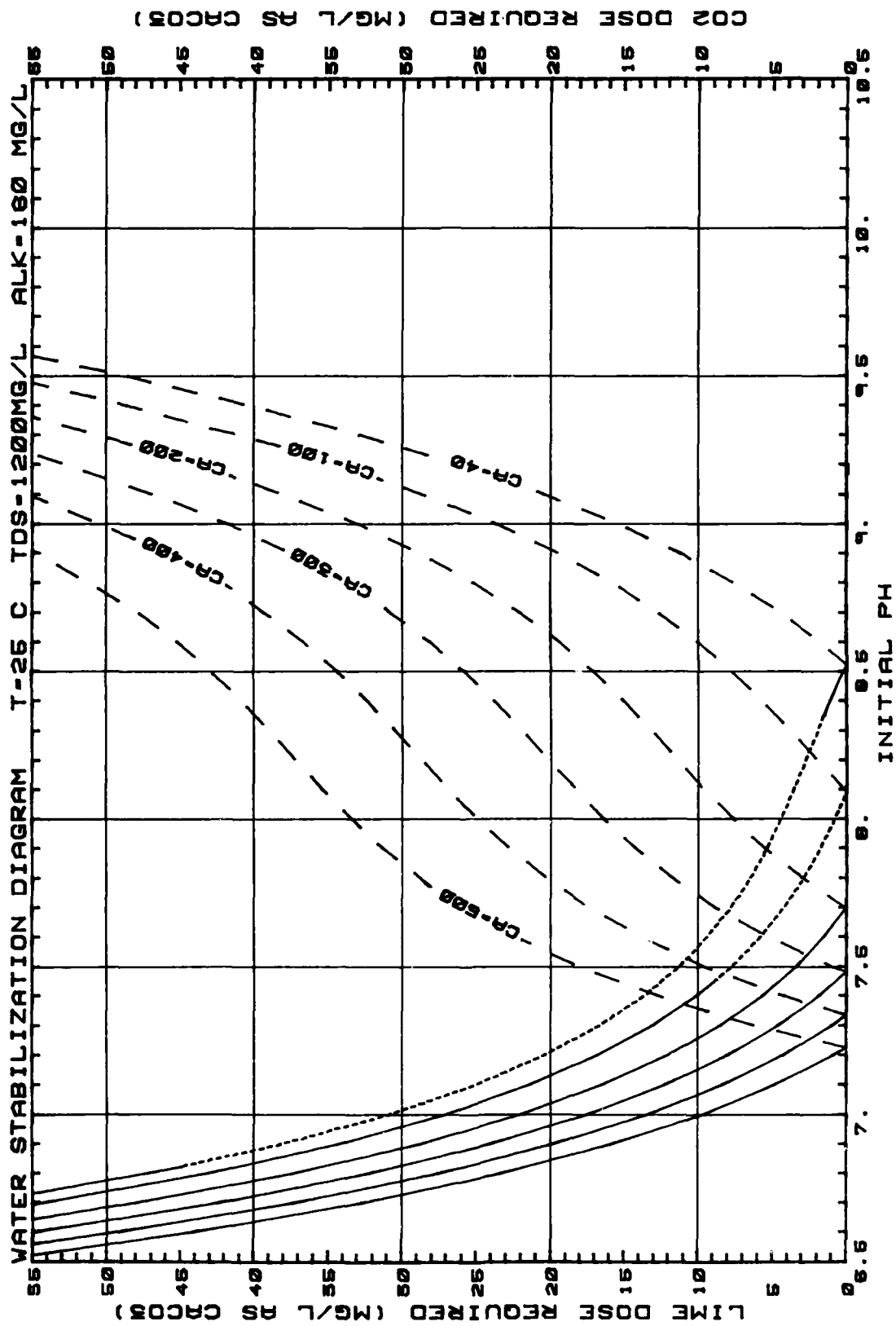


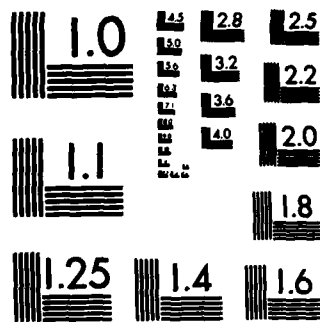
DIAGRAM A106

AD-A144 670

SIMPLIFIED PROCEDURE FOR CALCULATING CHEMICAL DOSES FOR 3/3
WATER STABILIZATI. (U) ARMY ENGINEER WATERWAYS
EXPERIMENT STATION VICKSBURG MS ENVIR.
J M MORGAN ET AL. JUN 84 WES/TR/EL-84-6 F/G 13/2 NL

UNCLASSIFIED

END



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

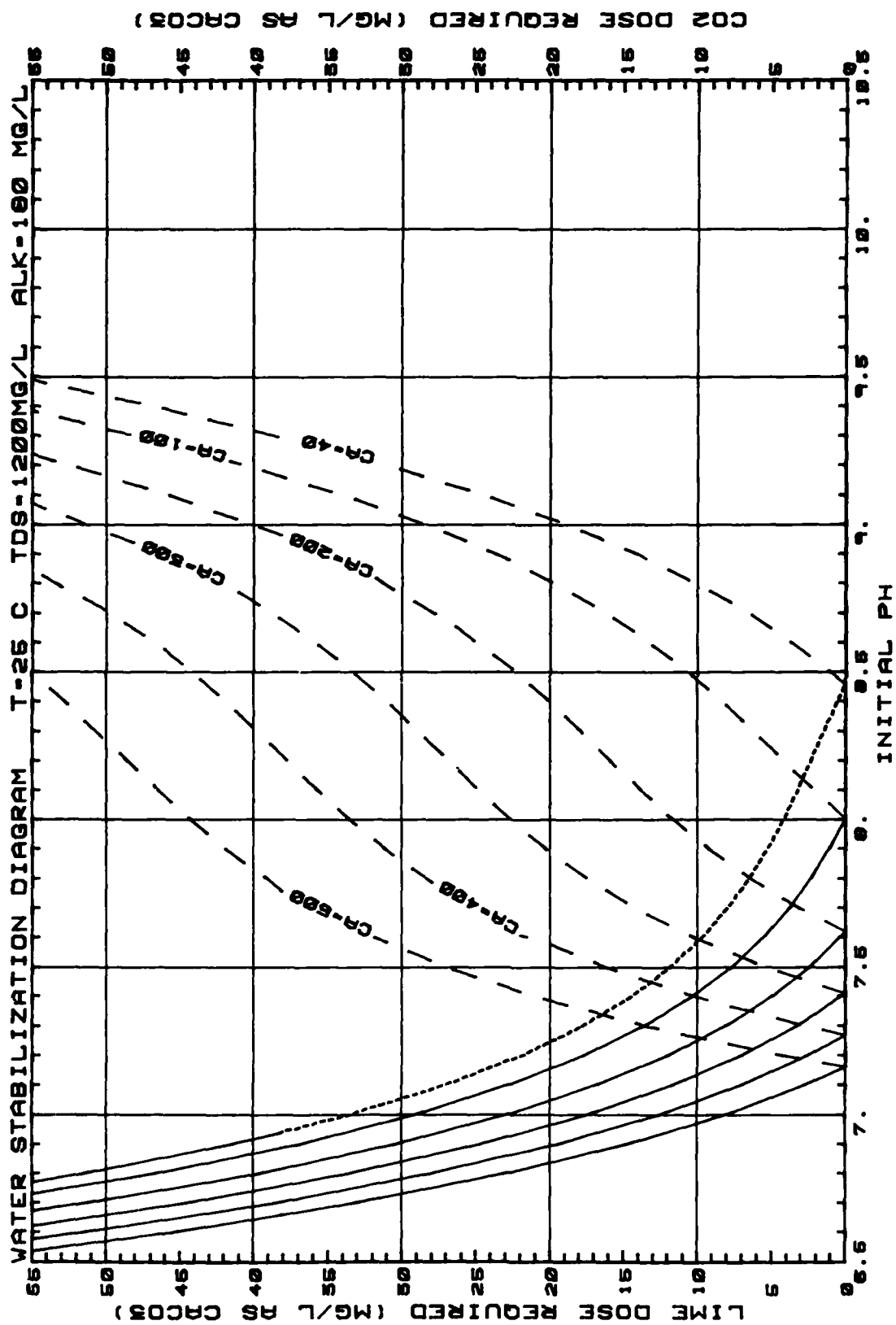


DIAGRAM A107

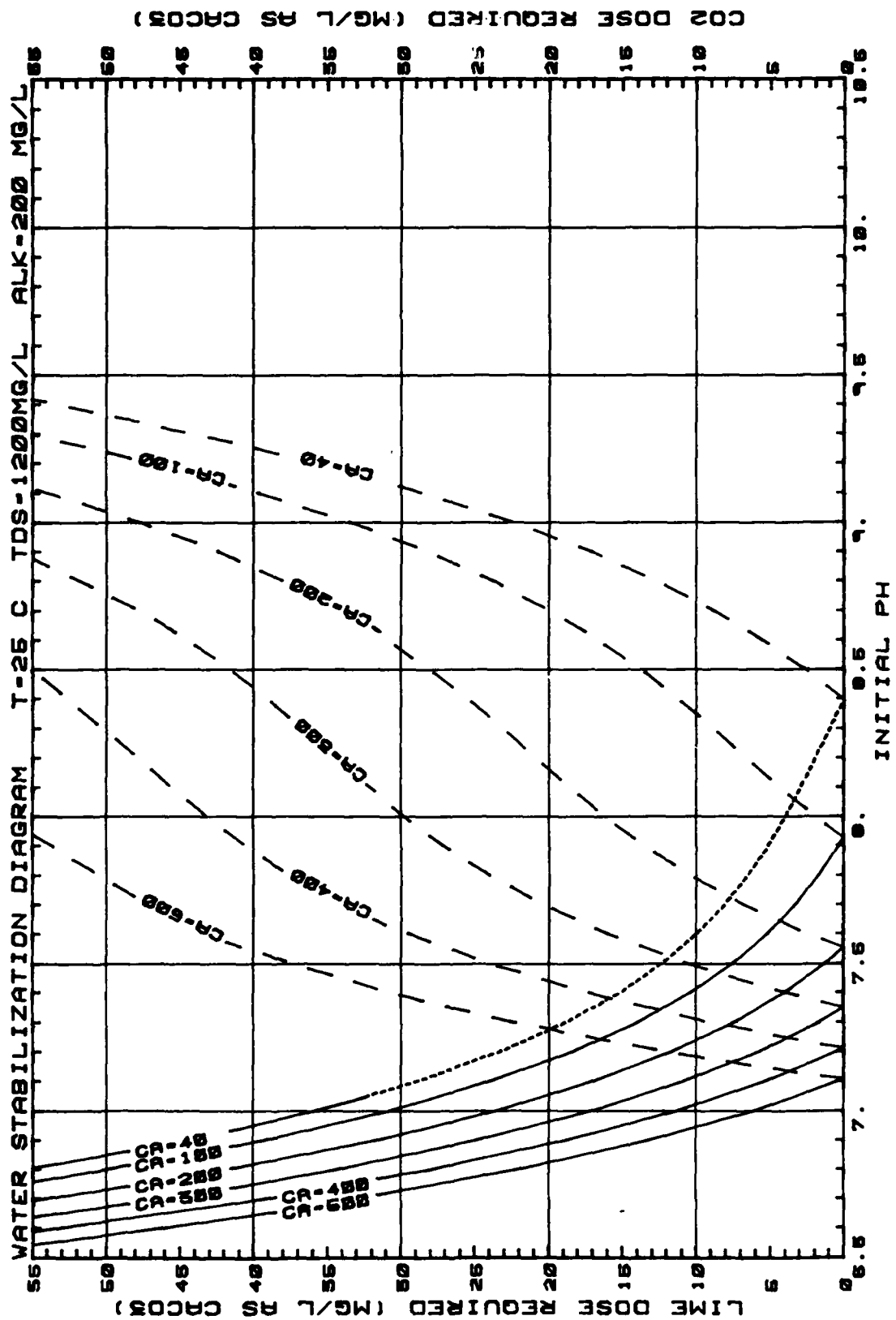


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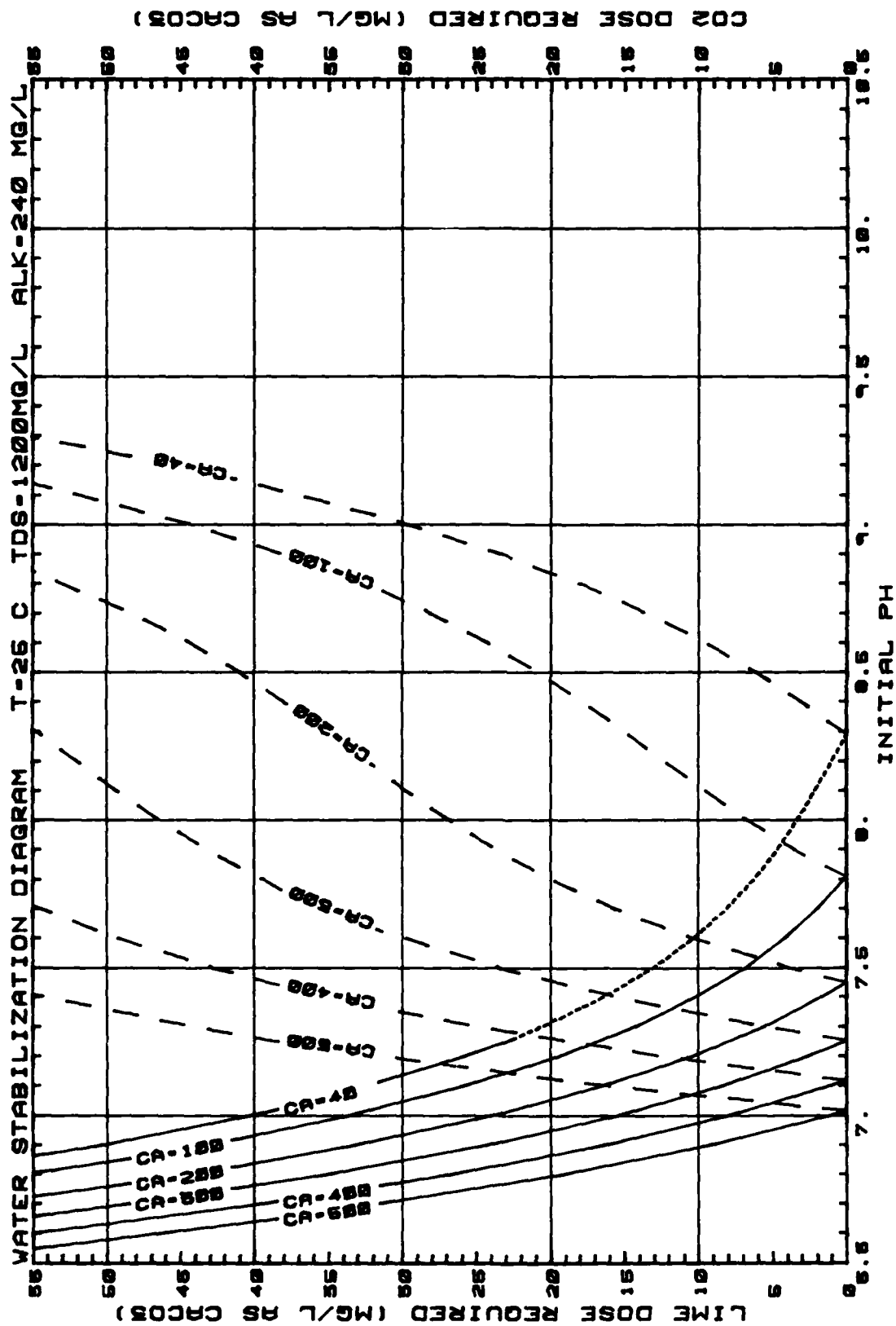


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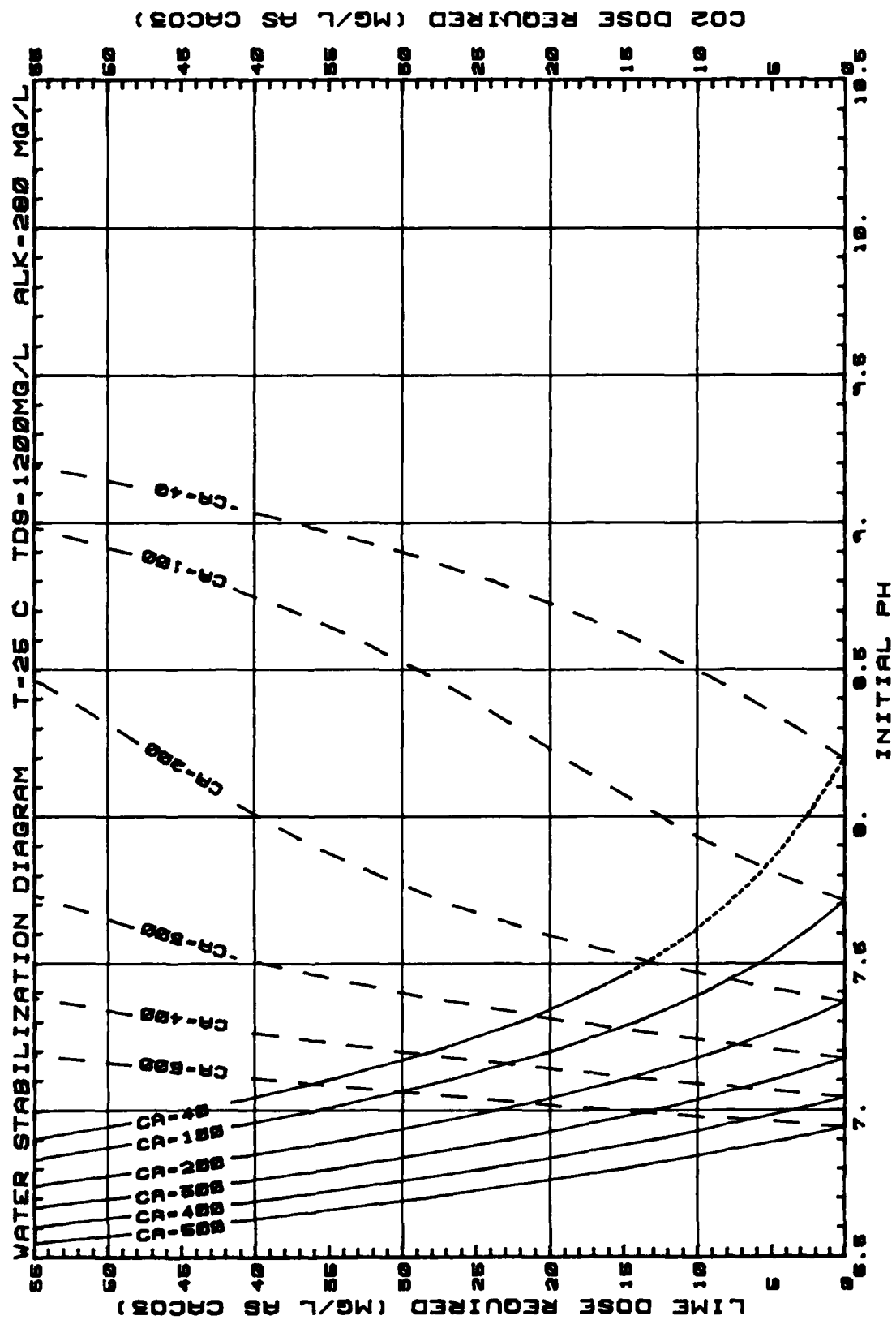


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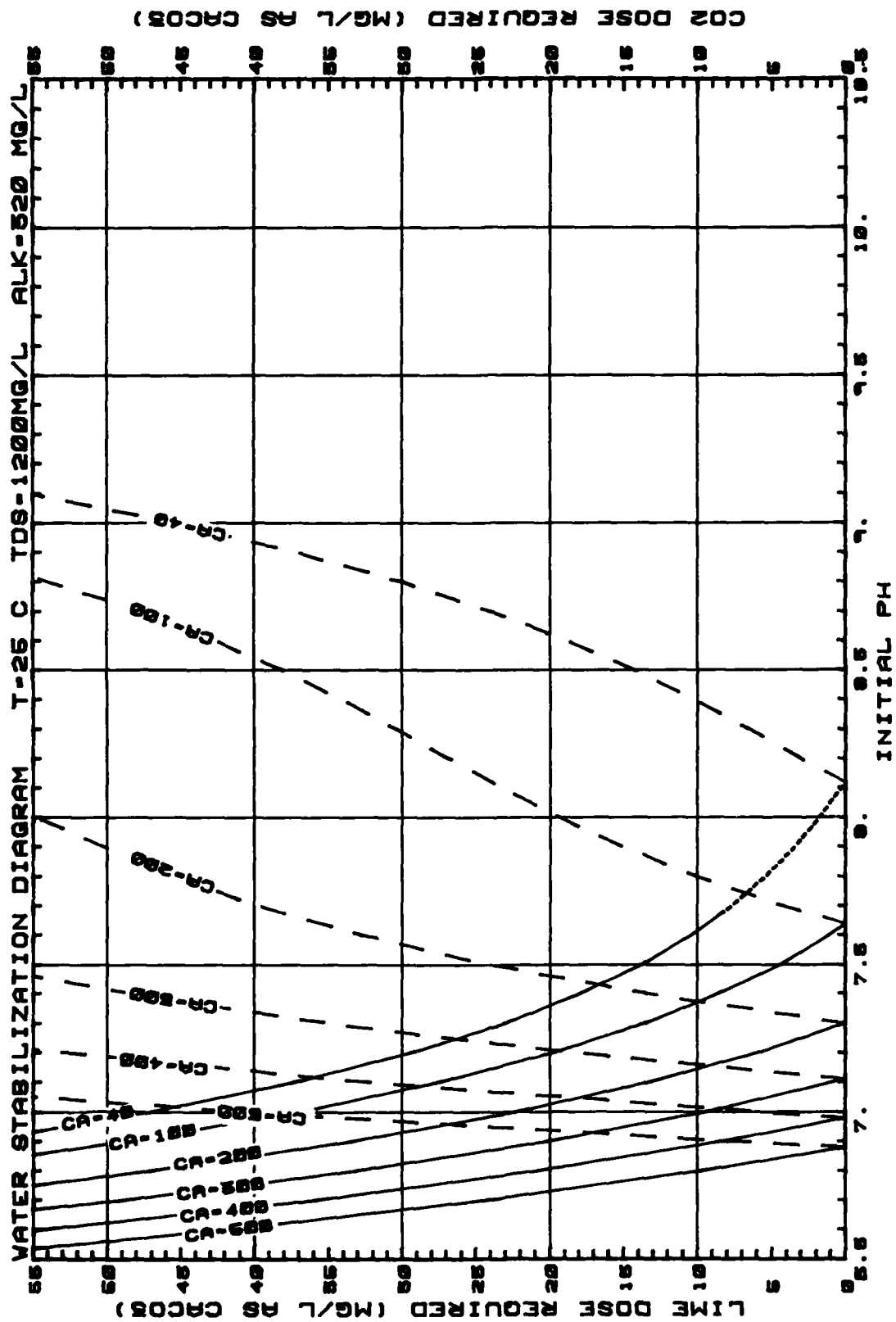


DIAGRAM A111

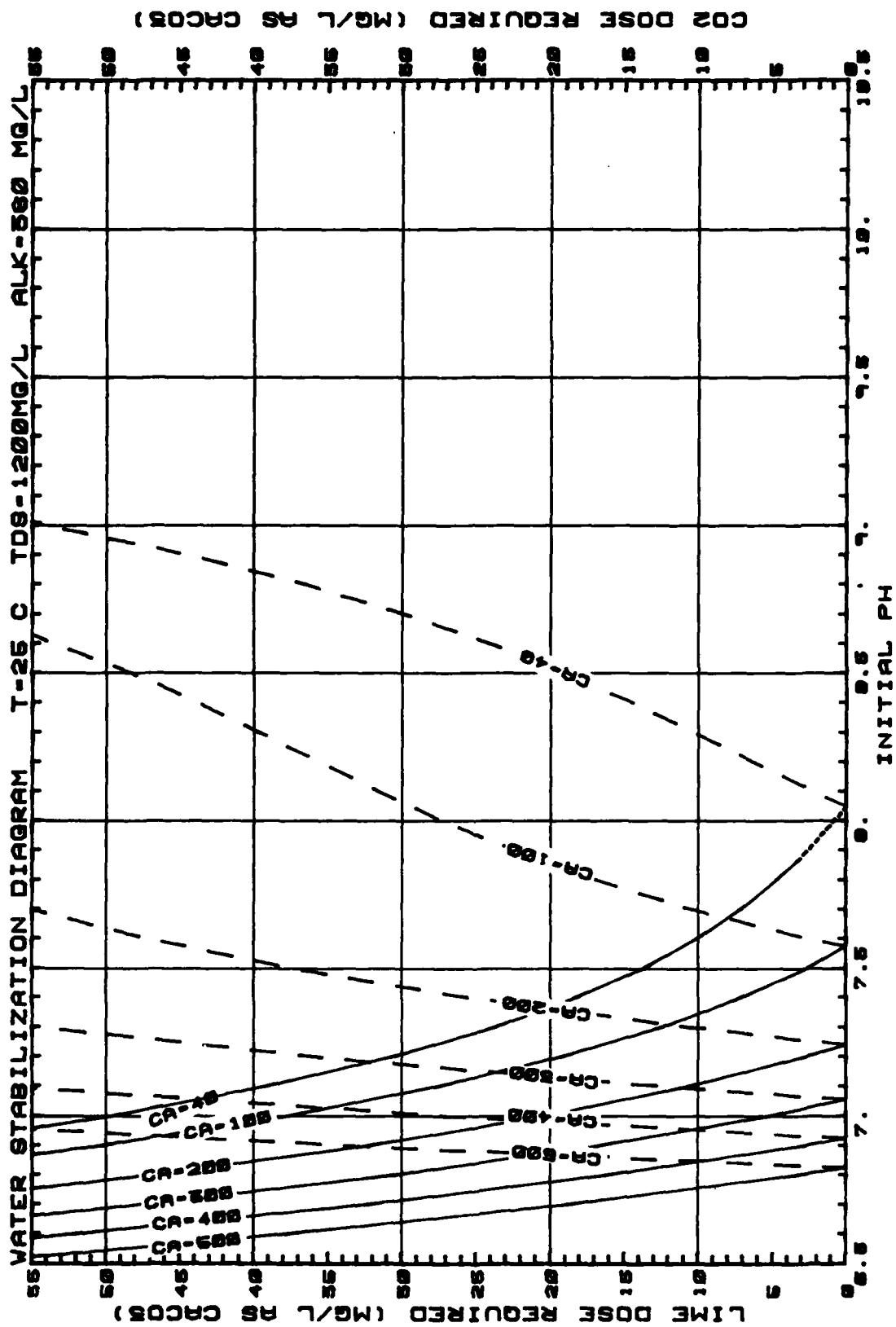


DIAGRAM A112

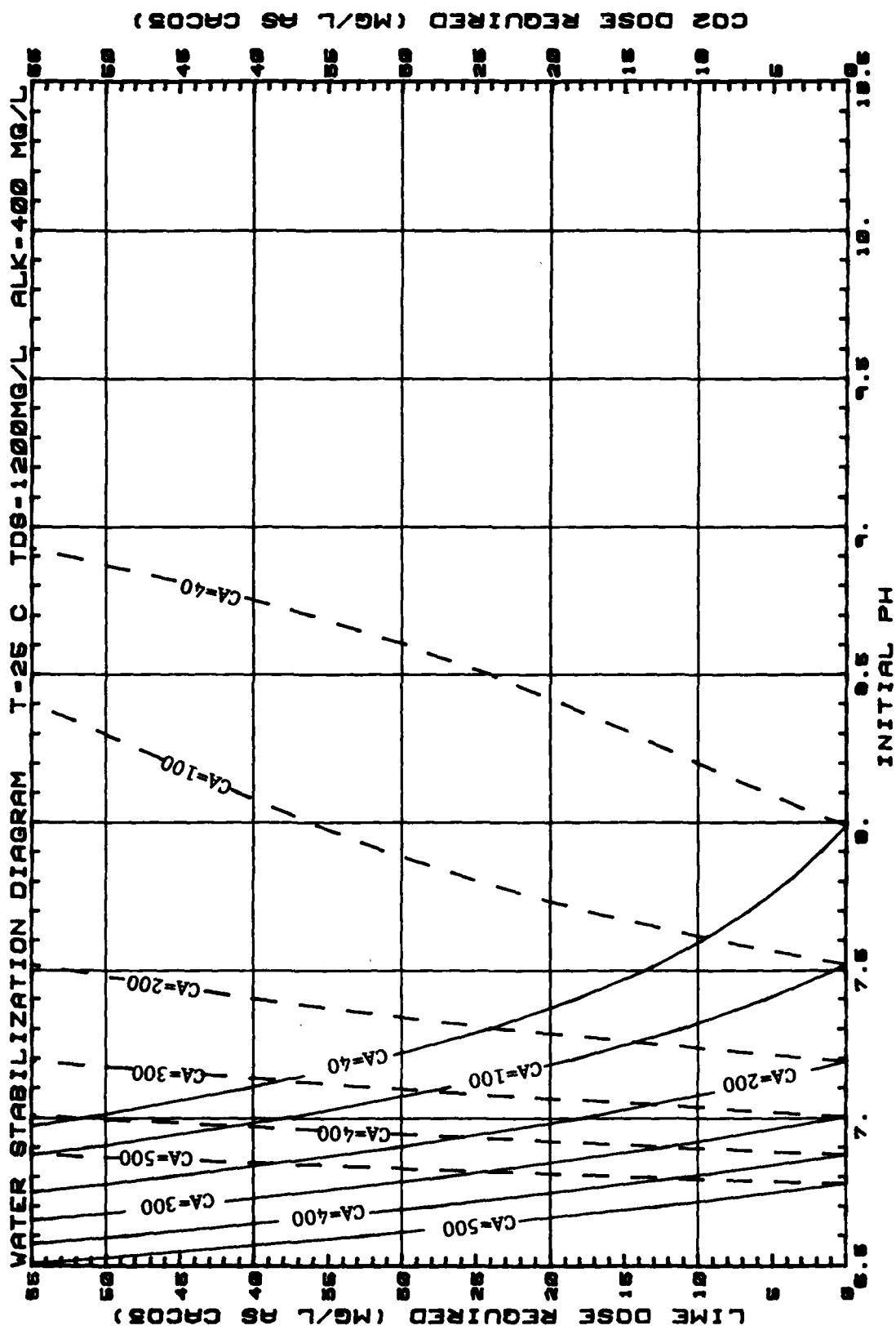


DIAGRAM A113

APPENDIX B: PROGRAM LISTING FOR THE IBM PERSONAL COMPUTER

```

10 REM WATER STABILIZATION PROGRAM
20 REM CLEAR SCREEN AND PRESENT TITLE SCREEN
30 REM
40 DIM V(20),B*(20):REM RETURN VARIABLES FROM THE FREE FORM ROUTINE
45 DIM SS(4)
50 COLOR 7,0
60 KEY OFF:CLS
70 LOCATE 2,27:PRINT "WATER STABILIZATION PROGRAM"
80 LOCATE 3,25:PRINT CHR$(219);:FOR I=27 TO 55:PRINT CHR$(220);:NEXT I:PRINT CHR
$(219);
90 LOCATE 1,25:PRINT CHR$(219);:FOR I=27 TO 55:PRINT CHR$(223);:NEXT I:PRINT CHR
$(219);
100 FOR I=2 TO 2:LOCATE I,25:PRINT CHR$(221);:NEXT I
110 FOR I=2 TO 2:LOCATE I,55:PRINT CHR$(222);:NEXT I
120 LOCATE 12,29:PRINT "ENVIRONMENTAL LABORATORY"
130 LOCATE 13,17:PRINT "U. S. ARMY ENGINEER WATERWAYS EXPERIMENT STATION"
140 LOCATE 14,32:PRINT "VICKSBURG, MISS."
150 LOCATE 11,15:PRINT CHR$(201);:FOR I=16 TO 65:PRINT CHR$(205);:NEXT I:PRINT C
HR$(187);
160 LOCATE 15,15:PRINT CHR$(200);:FOR I=16 TO 65:PRINT CHR$(205);:NEXT I:PRINT C
HR$(188);
170 FOR I=12 TO 14:LOCATE I,15:PRINT CHR$(186);:NEXT I
180 FOR I=12 TO 14:LOCATE I,66:PRINT CHR$(186);:NEXT I
190 COLOR 23,0
200 LOCATE 24,27:PRINT CHR$(219);:FOR I=28 TO 52:PRINT CHR$(220);:NEXT I:PRINT C
HR$(219);
210 LOCATE 22,27:PRINT CHR$(219);:FOR I=28 TO 52:PRINT CHR$(223);:NEXT I:PRINT C
HR$(219);
220 FOR I=23 TO 23:LOCATE I,27:PRINT CHR$(221);:NEXT I
230 FOR I=23 TO 23:LOCATE I,53:PRINT CHR$(222);:NEXT I
240 COLOR 7,0
250 LOCATE 23,30:PRINT "SPACE BAR TO CONTINUE";
260 A$=INKEY$:IF A$<>" " GOTO 260
270 CLS
275 FOR I=1 TO 4:SS(I)=0:NEXT I:KN=0
280 REM
290 REM PRESENT INPUT REQUEST SCREEN
300 REM T=TEMPERATURE - TD=TOTAL DISSOLVED SOLIDS - PR=DESIRED PRECIPITATE
310 REM AL=ALKALINITY - CA=CALCIUM - VA=INITIAL PH
320 REM
330 LOCATE 2,26:PRINT "WATER STABILIZATION PROGRAM"
335 XX=54
340 LOCATE 4,1:PRINT "TEMPERATURE?      DEGREES C"
350 LOCATE 6,1:PRINT "TOTAL DISSOLVED SOLIDS?      MG/L"
360 LOCATE 8,1:PRINT "DESIRED PRECIPITATE?      MG/L AS CaCO3"
370 LOCATE 10,1:PRINT "ALKALINITY?      MG/L AS CaCO3"
380 LOCATE 12,1:PRINT "CALCIUM?      MG/L AS CaCO3"
390 LOCATE 14,1:PRINT "INITIAL PH?"
400 COLOR 0,7:LOCATE 4,14:PRINT " ":LOCATE 4,14:LINE INPUT A$:LOCATE 4,14:COLOR
7,0:PRINT " ":LOCATE 4,14:PRINT A$:GOSUB 29930:T=V(1)
410 COLOR 0,7:LOCATE 6,25:PRINT " ":LOCATE 6,25:LINE INPUT A$:LOCATE 6,25:COLO
R 7,0:PRINT " ":LOCATE 6,25:PRINT A$:GOSUB 29930:TD=V(1)
420 COLOR 0,7:LOCATE 8,22:PRINT " ":LOCATE 8,22:LINE INPUT A$:LOCATE 8,22:COLOR
7,0:PRINT " ":LOCATE 8,22:PRINT A$:GOSUB 29930:PR=V(1)
430 COLOR 0,7:LOCATE 10,13:PRINT " ":LOCATE 10,13:LINE INPUT A$:LOCATE 10,13:C
OLOR 7,0:PRINT " ":LOCATE 10,13:PRINT A$:GOSUB 29930:AL=V(1)
440 COLOR 0,7:LOCATE 12,10:PRINT " ":LOCATE 12,10:LINE INPUT A$:LOCATE 12,10:C
OLOR 7,0:PRINT " ":LOCATE 12,10:PRINT A$:GOSUB 29930:CA=V(1)
450 LOCATE 14,37:COLOR 23,0:PRINT "STANDBY":COLOR 7,0
460 REM
470 REM CALCULATE CONSTANTS
480 REM IS=IONIC STRENGTH - G & GM=ACTIVITY COEFFICIENTS - A=f(T)
490 REM

```

```

500 IS=2.5*10^(-5)*TD
510 A=1.82*10^6*(78.3*(T+273))^(-1.5)
520 G=-A*(SQR(IS)/(1+SQR(IS))-.3*IS)
530 GM=10^(G):GD=10^(4*G)
540 REM
550 REM P1,P2,PW,PS,K1,K2,KW & KS=EQUILIBRIUM CONSTANTS
560 REM C1,C2,CW & CS CORRECTED FOR IONIC STRENGTH & TEMPERATURE-MG/L AS CaCO3
570 REM
580 P1=17052/(T+273)+215.21*LOG(T+273)/LOG(10)-.12675*(T+273)-545.56
590 P2=2902.39/(T+273)+.02379*(T+273)-6.498
600 PW=4787.3/(T+273)+7.1321*LOG(T+273)/LOG(10)+.010365*(T+273)-22.801
610 PS=.01183*T+8.03
620 K1=10^(-P1)
630 K2=10^(-P2)
640 KW=10^(-PW)
650 KS=10^(-PS)
660 C1=K1*25000/GM^2
670 C2=K2*100000!/GD
680 CW=KW*50000!^2/GM^2
690 CS=KS*100000!^2/GD^2
700 REM
710 REM CALCULATE SIGNIFICANT POINTS
720 REM LA=LIME ADDED - CO=CO2 ADDED
730 REM B6 & I6 ARE INITIAL PH AND INTERIM PH FOR LA=101.0 & CO=0
740 REM B0 & I0 ARE INITIAL PH AND INTERIM PH FOR LA=0 & CO=0
750 REM B8 IS INITIAL PH FOR INTERIM PH=8.0
760 REM F8 IS INITIAL PH FOR INTERIM PH=8.5
770 REM B9 IS INITIAL PH FOR INTERIM PH=9.2
780 REM BL & CL ARE PH AND CO2 ADDED FOR MAXIMUM PH
790 REM
795 LM=40-CA:IF 40-AL>LM THEN LM=40-AL
796 IF LM<0 THEN LM=0
800 LA=101!:CO=0:GOSUB 1210:I6=PI:B6=PH:LA=LM:GOSUB 1210:B0=PH:I0=PI
810 LA=101!
820 B8=B0:F8=B0:B9=B0
830 IF I0>8 THEN VA=8:GOSUB 1570:B8=PH
840 IF I0>8.5 THEN VA=8.5:GOSUB 1570:F8=PH
850 IF I0>9.2 THEN VA=9.2:GOSUB 1570:B9=PH
860 VA=B9:GOSUB 1480:GOSUB 1740:CL=CO:BL=PH
870 IF CL>101! THEN CO=101!:GOSUB 1210:CL=101!:BL=PH
880 REM OUTPUT PH RANGE AND INPUT THE INITIAL PH FOR THIS PROBLEM
890 LOCATE 14,19:PRINT USING "(PRACTICAL PH RANGE ###.## TO ###.##)":B6,BL
900 COLOR 0,7:LOCATE 14,13:PRINT " ":LOCATE 14,13:LINE INPUT A$:LOCATE 14,13:C
OLOR 7,0:PRINT " ":LOCATE 14,13:PRINT A$:GOSUB 29930:VA=V(1)
910 PRINT:PRINT "*****"
920 IF VA<B8 GOTO 960:REM ADD LIME - INTERIM PH < 8.0
930 IF VA<F8 GOTO 960:REM ADD LIME AND POSSIBLY CO2 - INTERIM PH IN RANGE 8-8.5
940 IF VA<B9 GOTO 1010:REM ADD LIME - INTERIM PH IN RANGE 8.5-9.2 OR < 8.0
950 GOTO 1030:REM ADD CO2 , ALSO LIME IF INTERIM PH>9.2
960 CO=0:GOSUB 1480:GOSUB 30230:IF VA<B8 GOTO 1110
970 PRINT "OR"
971 YY=CSRLIN:ZZ=POS(0)
972 XX=59:LOCATE 10,XX:PRINT USING "###.##":AF
974 LOCATE 12,XX:PRINT USING "###.##":CF
976 LOCATE 14,XX:PRINT USING "###.##":PF
978 LOCATE 10,65:PRINT "OR"
979 LOCATE YY,ZZ
980 VS=VA:VA=B8:GOSUB 1480:VA=VS
990 GOSUB 1660:GOSUB 30230
1000 GOTO 1110
1010 CO=0:GOSUB 1480:GOSUB 30230
1020 GOTO 1110
1030 VS=VA:VA=F8:GOSUB 1660:CO=C:VA=VS
1040 VS=VA:VA=B9:GOSUB 1480:VA=VS
1050 VS=VA:VA=B9:GOSUB 1480:VA=VS

```

```

1060 GOSUB 1660:GOSUB 30230
1070 GOTO 1110
1080 REM
1090 REM SOLUTION FINISHED - INQUIRE FOR APPROPRIATE ACTION
1100 REM
1110 LOCATE 24,1:PRINT CHR$(24);"PrtSc - HARD COPY: 'C'- FEED RATES: Space Bar
- NEXT PROBLEM: 'Q' - QUIT";
1111 XX=XX+9:YY=CSRLIN:ZZ=POS(0)
1112 LOCATE 8,60:PRINT "FINAL VALUES":LOCATE 10,XX:PRINT USING "###.##";AF
1114 LOCATE 12,XX:PRINT USING "###.##";CF:LOCATE 14,XX:PRINT USING "###.##";PF
1115 LOCATE YY,ZZ
1120 A$=INKEY$:IF A$=" " GOTO 270
1125 IF A$="C" GOTO 2000
1130 IF A$="Q" THEN END
1140 GOTO 1120
1150 REM
1160 REM CF=FINAL CALCIUM - AF=FINAL ALKALINITY - HF=FINAL H CONCENTRATION
1170 REM RA=RADICAL - AC=FINAL ACIDITY - AD=ORIGINAL ACIDITY
1180 REM AI=INTERIM ALKALINITY - CI=INTERIM CALCIUM
1190 REM H=ORIGINAL H CONCENTRATION - PH=ORIGINAL PH
1200 REM
1210 REM FIND PH AND PI FOR GIVEN LA AND CO
1220 REM
1230 CF=CA+LA-PR
1240 AF=AL+LA-PR
1250 RA=SQR((C2*CF/CS*(AF-CS/CF))^2-4*KW*C2*CF/CS)
1260 HF=.5*(C2*CF/CS*(AF-CS/CF)+RA)
1265 PH=-LOG(HF*GM/50000!)/LOG(10)
1267 PF=PH
1270 AC=(AF-CW/HF+HF)*((1+HF/C1)/(1+C2/HF)+HF-CW/HF)
1310 AD=AC+LA-CO
1320 GOSUB 1780
1330 PH=-LOG(H*GM/50000!)/LOG(10)
1340 REM
1350 AI=AL+LA:CI=AC
1360 GOSUB 1880
1420 PI=-LOG(H*GM/50000!)/LOG(10)
1430 RETURN
1440 REM
1450 REM NC=INCREMENTAL VALUE FOR ITERATION
1460 REM
1470 REM
1480 REM FIND INITIAL PH FOR VARYING LA: CO CONSTANT
1490 REM
1500 NC=10:LA=101!
1530 LA=LA-NC:GOSUB 1210:IF PH<VA GOTO 1530
1540 LA=LA+NC:NC=NC/10:IF ABS(NC-.001)<.002 THEN RETURN
1550 GOTO 1530
1560 REM
1570 REM FIND INTERIM PH FOR VARYING LA: CO CONSTANT
1580 REM
1590 NC=10:LA=101!
1620 LA=LA-NC:GOSUB 1210:IF PI<VA GOTO 1620
1630 LA=LA+NC:NC=NC/10:IF ABS(NC-.001)<.002 THEN RETURN
1640 GOTO 1620
1650 REM
1660 REM FIND PH FOR VARYING CO: LA CONSTANT
1670 REM
1680 CO=0:NC=10
1690 CO=CO+NC:GOSUB 1210:IF CO>101! THEN RETURN
1700 IF PH<VA THEN 1690
1710 CO=CO-NC:NC=NC/10:IF ABS(NC-.001)<.002 THEN RETURN
1720 GOTO 1690
1730 REM
1740 REM FIND UPPER LIMIT OF CO: LA CONSTANT
1750 REM

```



```

1760 CO=101!:GOSUB 1210
1770 RETURN
1780 HI=10^(-2):H=HI
1790 ZC=(AL-CW/H+H)*(1+H/C1)/(1+C2/H)+H-CW/H
1800 IF ABS(ZC-AD)<.01 THEN RETURN
1810 IF ZC>AD THEN H=H-HI:HI=HI/10:H=H+HI:GOTO 1790
1820 H=H+HI:GOTO 1790
1880 HI=10^(-2):H=HI
1890 ZC=(AI-CW/H+H)*(1+H/C1)/(1+C2/H)+H-CW/H
1900 IF ABS(ZC-CI)<.01 THEN RETURN
1910 IF ZC>CI THEN H=H-HI:HI=HI/10:H=H+HI:GOTO 1890
1920 H=H+HI:GOTO 1890
2000 CLS
2010 LOCATE 2,26:PRINT "WATER STABILIZATION PROGRAM"
2020 LOCATE 4,1:PRINT "PURITY: LIME?      %      CO2?      %"
2030 LOCATE 6,1:PRINT "FLOW RATE      MGD"
2040 COLOR 0,7:LOCATE 4,15:PRINT "      ":LOCATE 4,15:LINE INPUT A$:LOCATE 4,15:COLOR
R 7,0:PRINT "      ":LOCATE 4,15:PRINT A$:GOSUB 29930:LP=V(1)
2050 COLOR 0,7:LOCATE 4,28:PRINT "      ":LOCATE 4,28:LINE INPUT A$:LOCATE 4,28:COLOR
R 7,0:PRINT "      ":LOCATE 4,28:PRINT A$:GOSUB 29930:CP=V(1)
2060 COLOR 0,7:LOCATE 6,11:PRINT "      ":LOCATE 6,11:LINE INPUT A$:LOCATE 6,11:COLOR
R 7,0:PRINT "      ":LOCATE 6,11:PRINT A$:GOSUB 29930:QA=V(1)
2070 PRINT:PRINT "*****"
*****
2075 PRINT "AS COMMERCIALY AVAILABLE:"-PRINT
2080 C$="ADD ###.# MG/L OF LIME AS CA      ? : ###.# MG/L AS CAO"
2085 D$="ADD ###.# MG/L OF CO2 AS CO2"
2100 LA=SS(1)/LP*100:IF LA<>0! THEN PRINT USING C$;.74*LA,.56*LA
2110 CO=SS(2)/CP*100:IF CO<>0! THEN PRINT USING D$;.44*CO
2120 IF SS(3)=0 AND SS(4)=0 GOTO 2150
2125 PRINT "OR"
2130 LA=SS(3)/LP*100:IF LA<>0! THEN PRINT USING C$;.74*LA,.56*LA
2140 CO=SS(4)/CP*100:IF CO<>0! THEN PRINT USING D$;.44*CO
2150 PRINT:PRINT "*****"
*****
2155 PRINT "AS COMMERCIALY AVAILABLE:"-PRINT
2160 SS(1)=QA*8.34*SS(1)/LP*100/24:SS(2)=QA*8.34*SS(2)/CP*100/24
2170 SS(3)=QA*8.34*SS(3)/LP*100/24:SS(4)=QA*8.34*SS(4)/CP*100/24
2180 C$="ADD ###.# LB/HR OF LIME AS CA(OH)2 : ###.# LB/HR AS CAO"
2185 D$="ADD ###.# LB/HR OF CO2 AS CO2"
2200 LA=SS(1):IF LA<>0! THEN PRINT USING C$;.74*LA,.56*LA
2210 CO=SS(2):IF CO<>0! THEN PRINT USING D$;.44*CO
2220 IF SS(3)=0 AND SS(4)=0 GOTO 2500
2225 PRINT "OR"
2230 LA=SS(3):IF LA<>0! THEN PRINT USING C$;.74*LA,.56*LA
2240 CO=SS(4):IF CO<>0! THEN PRINT USING D$;.44*CO
2500 LOCATE 24,1:PRINT CHR$(24);"PrtSc - HARD COPY: Space Bar - NEXT PROBLEM: 'Q
' - QUIT";
2510 A$=INKEY$:IF A$=" " GOTO 270
2530 IF A$="Q" THEN END
2540 GOTO 2510
3000 END
29920 REM
29930 REM ***** FREE FORMAT ROUTINE
29940 REM THIS ROUTINE SCANS THE INPUT STRING A$ AND RETURN NUMERIC VALUES AND
29950 REM WORD LENGTH STRINGS IN V(I) AND B$(I) RESPECTIVLY.
29960 REM NW=NO OF WORDS - NN=NO OF NUMBERS
29970 REM WITH THE EXCEPTION OF NW, NN, A$ & B$ ALL VARIABLES IN THIS ROUTINE
29980 REM CONTAIN A 'Z'.
29990 REM
30000 FOR IZ=1 TO 20:B$(IZ)="":V(IZ)=0:NEXT IZ:VZ$="":A$=A$+" "
30010 NW=0:NN=0:NZ=0
30020 FOR IZ=1 TO LEN(A$)
30030 IZ$=MID$(A$,IZ,2):LZ$=LEFT$(IZ$,1):RZ$=RIGHT$(IZ$,1)
30040 IF NZ<>0 THEN 30150
30050 IF LZ$=" " THEN 30180

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30060 IF LZ$="0" THEN 30110
30070 IF LZ$="+" THEN 30110
30080 IF LZ$="-" THEN 30110
30090 IF LZ$="." THEN 30110
30100 IF LZ$<"1" OR LZ$>"9" GOTO 30130
30110 VZ$=VZ$+LZ$:IF RZ$<>" " THEN 30180
30120 NN=NN+1:V(NN)=VAL(VZ$):VZ$="":GOTO 30180
30130 IF NZ<>0 THEN 30150
30140 B$(NW+1)=LZ$:NZ=1:GOTO 30160
30150 B$(NW+1)=B$(NW+1)+LZ$
30160 IF RZ$<>" " THEN 30180
30170 NW=NW+1:NZ=0
30180 NEXT IZ
30190 RETURN
30200 REM
30210 REM PRINT RESULTS
30220 REM
30230 C$="ADD ###.# MG/L OF LIME AS CaCO3 : ###.# MG/L AS Ca(OH)2 : ###.# MG/L A
S CaO"
30240 D$="ADD ###.# MG/L OF CO2 AS CaCO3 : ###.# MG/L AS CO2"
30250 KN=KN+1:SS(KN)=LA:IF LA<>0! THEN PRINT USING C$;LA,.74*LA,.56*LA
30260 KN=KN+1:SS(KN)=CO:IF CO<>0! THEN PRINT USING D$;CO,.44*CO
30270 PRINT USING "INTERIM PH WILL BE ##.##";PI
30280 RETURN

```

APPENDIX C: PROGRAM LISTING FOR THE APPLE II COMPUTER

LIST

```

10 REM WATER CONDITIONING PROGRAM
20 REM CLEAR SCREEN AND PRESENT TITLE SCREEN
30 REM
40 DIM V(20),B$(20): REM RETURN VARIABLES FROM FREE FORMAT ROUTINE
45 DIM SS(4),QS(4)
50 INPUT "DO YOU WANT HARD COPY(Y/N)?":P$
55 PR# 0
60 IF P$ = "Y" THEN PR# 1
65 HOME
68 VTAB 6: PRINT "*****"
70 VTAB 8: PRINT TAB( 7)"WATER CONDITIONING PROGRAM"
120 VTAB 12: PRINT TAB( 9)"ENVIRONMENTAL LABORATORY"
130 VTAB 16: PRINT "U.S. ARMY WATERWAYS EXPERIMENT STATION"
140 VTAB 20: PRINT TAB( 13)"VICKSBURG, MISS."
250 VTAB 23: PRINT TAB( 11)"RETURN TO CONTINUE"
260 GET AN$
270 HOME
275 FOR I = 1 TO 4:SS(I) = 0: NEXT I:KN = 0
280 REM
290 REM PRESENT INPUT REQUEST SCREEN
300 REM T=TEMPERATURE DEG C
301 REM TD=TOTAL DISSOLVED SOLIDS MG/L
302 REM PR=DESIRED PRECIPITATE MG/L
303 REM AL=ALKALINITY MG/L
304 REM CA=CALCIUM MG/L
305 REM VA=INITIAL PH
306 REM ALL CONCENTRATIONS AS CaCO3
320 REM
325 IF P$ = "Y" THEN PR# 1
330 VTAB 3: PRINT TAB( 7)"WATER CONDITIONING PROGRAM"
340 PRINT : INPUT "TEMPERATURE(DEG C)?":T
350 PRINT : INPUT "TOTAL DISSOLVED SOLIDS(MG/L)?":TD
360 PRINT : INPUT "DESIRED PRECIPITATE(MG/L AS CaCO3)?":PR
370 PRINT : INPUT "ALKALINITY(MG/L AS CaCO3)?":AL
380 PRINT : INPUT "CALCIUM(MG/L AS CaCO3)?":CA
400 FLASH
450 VTAB (23): PRINT "STANDBY"
451 NORMAL
460 REM
470 REM CALCULATING CONSTANTS
480 REM IS=IONIC STRENGTH
490 REM G&GR = ACTIVITY COEFFICIENTS
495 REM
500 IS = 2.5 * 10 ^ ( - 5) * TD
510 A = 1.82 * 10 ^ 6 * (78.3 * (T + 273)) ^ ( - 1.5)
520 G = - A * ( SQR (IS) / (1 + SQR (IS)) - .3 * IS)
530 GM = 10 ^ (G)
535 GD = 10 ^ (4 * G)
540 REM
550 REM P1,P2,PW,PS,K1,K2,KW,KS=EQUILIBRIUM CONSTANTS
560 REM C1,C2,CW,&CS CONSTANTS CORRECTED FOR
561 REM IONIC STRENGTH AND TEMPERATURE
570 REM
580 P1 = 17052 / (T + 273) + 215.21 * LOG (T + 273) / LOG (10) - .12675 * (T +
273) - 545.56
590 P2 = 2902.39 / (T + 273) + .02379 * (T + 273) - 6.498
600 PW = 4787.3 / (T + 273) + 7.1321 * LOG (T + 273) / LOG (10) + .010365 * (T
+ 273) - 22.801
610 PS = .01183 * T + 8.03
620 K1 = 10 ^ ( - P1)
630 K2 = 10 ^ ( - P2)

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640 KW = 10 ^ ( - PW)
650 KS = 10 ^ ( - PS)
660 C1 = K1 * 25000 / GM ^ 2
670 C2 = K2 * 100000 / GD
680 CW = KW * 50000 ^ 2 / GM ^ 2
690 CS = KS * 100000 ^ 2 / GD ^ 2
700 REM
710 REM CALCULATE SIGNIFICANT POINTS
720 REM LA=LIME ADDED
725 REM CO=CO2 ADDED
730 REM B6 & I6 ARE INTIIAL AND INTERIM PH FOR LA=60 & CO=0
740 REM B0 & I0 ARE INITIAL AND INTERIM PH FO LA=0 & CO=0
750 REM B8 IS INITIAL PH FOR INTERIM PH=8.0
760 REM F8 IS INITIAL PH FOR INTERIM PH=8.5
770 REM B9 IS INITIAL PH FOR INTERIM PH=9.2
780 REM BL & CL ARE PH AND CO2 ADDED FOR MAXIMUM PH
790 REM
795 LM = 40 - CA: IF 40 - AL > LM THEN LM = 40 - AL
796 IF LM < 0 THEN LM = 0
800 LA = 101:CO = 0: GOSUB 1210:I6 = PI
805 B6 = PH:LA = LM: GOSUB 1210:B0 = PH:I0 = PI
810 LA = 101
820 B8 = B0:F8 = B0:B9 = B0
830 IF I0 > 8 THEN VA = 8: GOSUB 1570:B8 = PH
840 IF I0 > 8.5 THEN VA = 8.5: GOSUB 1570:F8 = PH
850 IF I0 > 9.2 THEN VA = 9.2: GOSUB 1570:B9 = PH
860 VA = B9: GOSUB 1480: GOSUB 1740:CL = CO:BL = PH
870 IF CL > 101 THEN CO = 101: GOSUB 1210:CL = 101:BL = PH
880 REM OUTPUT PH RANGE AND INPUT THE INITIAL PH RANGE FOR THIS PROBLEM
890 NORMAL : VTAB (23): PRINT "ALLOWABLE PH RANGE ";B6;" TO ";BL
900 INPUT "INITIAL PH?";VA
910 PRINT : PRINT "*****": FLASH : PRINT "STANDBY": NORMAL
920 IF VA < B8 GOTO 960: REM ADD LIME - INTERIM PH<8
930 IF VA < F8 GOTO 960: REM ADD LIME AND MAYBE CO2 - INTERIM PH IN 8 - 8.5 RA
NBE
940 IF VA < B9 GOTO 1010: REM ADD LIME - INTERIM PH IN 8.2-9 RANGE OR < 8.0
950 GOTO 1030: REM ADD CO2 - ALSO LIME IF INTERIM PH >9.2
960 CO = 0: GOSUB 1480: GOSUB 2135: IF VA < B8 GOTO 1110
970 PRINT "OR"
980 VS = VA:VA = B8: GOSUB 1480:VA = VS
990 GOSUB 1660: GOSUB 2135
1000 GOTO 1110
1010 CO = 0: GOSUB 1480: GOSUB 2135
1020 GOTO 1110
1030 VS = VA:VA = F8: GOSUB 1660:CO = 0:VA = VS
1040 VS = VA:VA = F8: GOSUB 1480:VA = VS
1050 VS = VA:VA = B9: GOSUB 1480:VA = VS
1060 GOSUB 1660: GOSUB 2135
1070 GOTO 1110
1080 REM
1090 REM SOLUTION FINISHED - QUESTION FOR OUTPUT
1100 REM
1110 PRINT : INPUT "TYPE Q TO QUIT - C FOR CHEM FEED - RETURN FOR NEW PROBLEM?"
"A$
1120 IF A$ = "Q" THEN END
1130 IF A$ = "C" GOTO 1930
1140 GOTO 270
1150 REM
1160 REM CF=FINAL CALCIUM
1161 REM AF=FINAL ALKALINITY
1162 REM HF=FINAL H ION CONC
1170 REM RA=RADICAL
1171 REM AC=FINAL ACIDITY
1172 REM AD=ORIGINAL ACIDITY
1180 REM AI=INTERIM ALKALINITY
1181 REM CI=INTERIM CALCIUM

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1190 REM H=ORIGINAL H ION CONC
1191 REM PH=ORIGINAL PH
1200 REM
1210 REM FIND PH AND PI GIVEN LA AND CO
1220 REM
1230 CF = CA + LA - PR
1240 AF = AL + LA - PR
1249 IF CF < = 0 THEN CF = .1
1250 RA = SQR ((C2 * CF / CS * (AF - CS / CF)) ^ 2 - 4 * KW * C2 * CF / CS)
1260 HF = .5 * (C2 * CF / CS * (AF - CS / CF) + RA)
1265 PH = - LOG (HF * GM / 50000) / LOG (10)
1267 PF = PH
1270 AC = (AF - CW / HF + HF) * (1 + HF / C1) / (1 + C2 / HF) + HF - CW / HF
1310 AD = AC + LA - CO
1320 GOSUB 1780
1330 PH = - LOG (H * GM / 50000) / LOG (10)
1340 REM
1350 AI = AL + LA:CI = AC
1360 GOSUB 1880
1420 PI = - LOG (H * GM / 50000) / LOG (10)
1430 RETURN
1440 REM
1450 REM NC=INCREMENTAL VALUE FOR ITERATION
1460 REM
1480 REM FIND INITIAL PH GIVEN LA: CO CONSTANT
1490 REM
1500 NC = 10:LA = 101
1530 LA = LA - NC: GOSUB 1210: IF PH < VA GOTO 1530
1540 LA = LA + NC:NC = NC / 10: IF ABS (NC - .001) < .002 THEN RETURN
1550 GOTO 1530
1560 REM
1570 REM FIND INTERIM PH GIVEN LA: CO CONSTANT
1580 REM
1610 NC = 10:LA = 101
1620 LA = LA - NC: GOSUB 1210: IF PI < VA GOTO 1620
1630 LA = LA + NC:NC = NC / 10: IF ABS (NC - .001) < .002 THEN RETURN
1640 GOTO 1620
1650 REM
1660 REM FIND PH FOR VARYING CO: LA CONSTANT
1670 REM
1680 CO = 0:NC = 10
1690 CO = CO + NC: GOSUB 1210: IF CO > 101 THEN RETURN
1700 IF PH < VA GOTO 1690
1710 CO = CO - NC:NC = NC / 10: IF ABS (NC - .001) < .002 THEN RETURN
1720 GOTO 1690
1730 REM
1740 REM FIND UPPER LIMIT OF CO:LA CONSTANT
1750 REM
1760 CO = 101: GOSUB 1210
1770 RETURN
1780 HI = 10 ^ ( - 2):H = HI
1790 ZC = (AL - CW / H + H) * (1 + H / C1) / (1 + C2 / H) + H - CW / H
1800 IF ABS (ZC - AD) < .01 THEN RETURN
1810 IF ZC > AD THEN H = H - HI:HI = HI / 10:H = H + HI: GOTO 1790
1820 H = H + HI: GOTO 1790
1880 HI = 10 ^ ( - 2):H = HI
1890 ZC = (AI - CW / H + H) * (1 + H / C1) / (1 + C2 / H) + H - CW / H
1900 IF ABS (ZC - CI) < .01 THEN RETURN
1910 IF ZC > CI THEN H = H - HI:HI = HI / 10:H = H + HI: GOTO 1890
1920 H = H + HI: GOTO 1890
1930 HOME
1940 PRINT TAB( 7)"WATER CONDITIONING PROGRAM"
1950 PRINT : INPUT "PURITY LIME(%)"?;LP
1960 PRINT : INPUT "PURITY CO2(%)"?;CP
1970 PRINT : INPUT "FLOW RATE(MGD)"?;QA
1975 PRINT "*****"

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1980 PRINT "AS COMMERCIALY AVAILABLE": PRINT
1985 LA = SS(1):CO = SS(2)
1990 LQ = LA * .56 * 100 / LP:LH = LQ * .74 / .56
2000 IF SS(1) < = 0 GOTO 2006
2002 PRINT "ADD ";LQ;" MG/L OF LIME AS CAO"
2004 PRINT "ADD ";LH;" MG/L OF LIME AS CA(OH)2"
2006 IF SS(2) < = 0 OR CP < = 0 GOTO 2012
2008 CX = SS(2) * 44 / CP
2010 PRINT : PRINT "ADD ";CX;" MG/L AS CO2"
2012 IF SS(3) = 0 AND SS(4) = 0 GOTO 2020
2014 PRINT "OR":LQ = SS(3) * 56 / LP:LH = LQ * .64 / .56
2015 IF SS(3) < = 0 GOTO 2018
2016 PRINT "ADD ";LQ;" MG/L OF LIME AS CAO"
2017 PRINT "ADD ";LH;" MG/L OF LIME AS CA(OH)2"
2018 CX = SS(4) * 44 / CP: IF SS(4) < = 0 GOTO 2020
2019 PRINT : PRINT "ADD ";CX;" MG/L AS CO2"
2020 IF QA = 0 THEN GOTO 2080
2022 PRINT "*****"
2023 PRINT "FEED RATE OF COMMERCIAL CHEMICAL"
2025 QS(1) = SS(1) * QA * 834 / LP / 24:QS(2) = SS(2) * QA * 834 / CP / 24
2026 QS(3) = SS(3) * QA * 834 / LP / 24:QS(4) = SS(4) * QA * 834 / CP / 24
2030 IF SS(1) < = 0 GOTO 2035
2031 PRINT : PRINT "ADD ";QS(1) * .56;" LB/HR OF LIME AS CAO"
2032 PRINT : PRINT "ADD ";QS(1) * .74;" LB/HR OF LIME AS CA(OH)2"
2035 IF SS(2) < = 0 GOTO 2038
2036 PRINT : PRINT "ADD ";QS(2) * .44;" LB/HR OF CO2 AS CO2"
2038 IF QS(3) > 0 OR QS(4) > 0 THEN PRINT "OR"
2040 IF SS(3) < = 0 GOTO 2050
2041 PRINT : PRINT "ADD ";QS(3) * .56;" LB/HR OF LIME AS CAO"
2045 PRINT : PRINT "ADD ";QS(3) * .74;" LB/HR AS CA(OH)2"
2050 IF SS(4) < = 0 GOTO 2080
2051 PRINT : PRINT "ADD ";QS(4) * .44;" LB/HR OF CO2 AS CO2"
2080 INPUT "TYPE Q TO QUIT - RETURN FOR NEXT PROBLEM? ";A$
2090 IF A$ = "Q" THEN END
2100 GOTO 270
2110 REM
2120 REM PRINT RESULTS
2130 REM
2135 IF KN = 0 THEN HOME : PRINT "CHEMICAL DOSAGE BASED ON PURE CHEMICAL": PRI
NT
2138 IF LA < .02 THEN LA = 0
2139 KN = KN + 1:SS(KN) = LA
2140 IF LA < > 0 THEN PRINT "ADD ";LA;" MG/L OF LIME AS CAC03"
2145 KN = KN + 1:SS(KN) = CO
2150 IF CO < > 0 THEN PRINT "ADD ";CO;" MG/L OF CO2 AS CAC03"
2160 PRINT "INTERIM PH WILL BE ";PI
2162 PRINT : PRINT "FINAL CA ";CF;" MG/L AS CAC03"
2164 PRINT : PRINT "FINAL ALK ";AF;" MG/L AS CAC03"
2166 PRINT : PRINT "FINAL PH ";PF
2170 RETURN

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END

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